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(54) Title: PROCESS FOR PRODUCING AND UTILIZING AN OXYGEN ENRICHED GAS

(57) Abstract

This invention comprises a method and apparatus for obtaining from air (2) an oxygen enriched gas mixture containing at least 40 mole % nitrogen. The apparatus comprises a gas turbine, an oxygen separation unit which is in fluid communication with the turbine air compressor (28) and means for maintaining a proper mass balance tolerance between the turbine compressor/unit and the turbine energy production unit (26). This invention comprises a method and apparatus for recovering large quantities of an oxygen enriched gas from the volume of a compressed air stream (10) produced by a gas turbine by compensation of the mass loss to the energy production unit section (26) thereof by providing means for maintaining the turbine in proper mass and thermal balance as the turbine is utilized to provide the duty/ power requirements of a process which utilizes the oxygen enriched gas stream as a reactant.

APPLICATION FOR PATENT

TITLE: PROCESS FOR PRODUCING AND UTILIZING AN
          OXYGEN ENRICHED GAS

SPECIFICATION

FIELD OF THE INVENTION

          This invention relates to a process and
apparatus for the production of low cost oxygen
enriched air in large volume which may be used for
5   converting carbonaceous starting materials like
natural gas, naphtha, heavy oil, and solid
carbonaceous materials like coal to a raw synthesis-
gas having a substantial content of nitrogen, and to
processes for converting such nitrogen containing
10   raw synthesis gas to recoverable products,
preferably to normally liquid carbon containing
compounds which are suitable for fuel use or
synthetic gasoline.

15   BACKGROUND OF THE INVENTION

          Natural gas resources are located in many areas
which are remote from means for transporting such
natural gas conveniently and/or economically to a
market. In many remote locations the natural gas is
20   co-produced with crude oil and must be disposed of,
by flaring or reinjection, in order to produce the
crude. Flaring has become an unacceptable disposal
method since it wastes a diminishing hydrocarbon
resource and is also a source of air pollution.
25   Reinjection, which adds to the cost of crude oil

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production, is often unacceptable both in view of
its cost and the adverse effects it may impose upon
crude oil production from the field itself.
The inability to dispose of natural gas produced in
5   association with crude at a remote location in a
manner which is economically, governmentally and
environmentally acceptable has brought crude oil
production at some locations to a halt.

     Carbon containing compositions, such as coal
10   and natural gas, may be converted to other useful
hydrocarbon forms by first converting the carbon
composition to a synthesis gas. A synthesis gas is
one containing at least hydrogen (H_2) and carbon
monoxide (CO). A synthesis gas may be reacted over
15   a variety of catalysts under various conditions to
cause the H_2 and CO content thereof to react to form
a variety of carbon containing compounds ranging
from methanol (CH_3OH), dimethyl ether (DME), normally
liquid hydrocarbons, etc. Methods for the
20   production of synthetic gasoline and diesel fuel,
whether by Fischer-Tropsch technology or by the
Methanol to Gasoline (MTG) technology developed by
Mobil, all require the production of a synthesis
gas.

25   Two basic methods are employed to convert a
carbon source to a synthesis gas, namely steam
reforming or by adiabatic reaction of the carbon
with an amount of oxygen less than the
stoichiometric quantity required for complete carbon
30   oxidation. Adiabatic reforming is the only possible
method for materials boiling higher than naphtha.

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For natural gas and heavier material, up to naphtha,
steam reforming (commonly over a nickel-containing
catalyst) is the preferred method. Especially for
ammonia production, but also in other cases, -

5   adiabatic reforming over such a nickel catalyst is
also often practiced. The preparation of a
synthesis gas by steam reforming non-adiabatically,
that is with a large heat input, is a process
attendant with large capital and high operating

10   cost. Partial oxidation with or without catalyst
present produces a synthesis gas of a lower hydrogen
content than does steam reforming. In order to
avoid the introduction of large amounts of nitrogen
(N_2) as an inert diluent into the system (which is a

15   desire for all targeted uses of synthesis gas, with
the exception of production of ammonia), essentially
pure oxygen must be used. Accordingly, production
of an essentially nitrogen free synthesis gas by
adiabatic reforming is also an intensive capital and

20   operating cost process since an oxygen separation
unit is required together with compressors of
special construction required for the safe
compression of gases containing 35 mole % or greater
oxygen. Adiabatic reforming is generally employed

25   in order to provide an operator flexibility for
using different carbon feedstocks ranging form
natural gas to readily volatizable hydrocarbon
compounds.

       Many proposals have been set forth for

30   processes which would recover remote location
natural gas in a normally liquid hydrocarbon form by

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converting it on location to a synthesis gas and
then processing such synthesis gas by known methods
to convert it to methanol or to other liquid
hydrocarbon forms. Since the world market for
5   methanol is insufficient to accommodate that
quantity of methanol which would result by recovery
of remote natural gas in this form, this manner of
resolving the problem has not yet been practiced.

     With the development in the mid 1970's by Mobil
10   of a catalytic process for the conversion of methoxy
containing compounds, such as methanol and DME, to
gasoline grade liquid hydrocarbons, it appeared
conceivable to recover remote natural gas on site in
the form of a normally liquid hydrocarbon.

15   Such processes are intensive in their capital
and operating cost, in large part due to the manner
by which the natural gas is reformed to a synthesis
gas and the need to match the synthesis gas
pressure to the conditions required for its
20   conversion to methanol and then to gasoline in the
Mobil MTG process. Nevertheless, as crude oil
prices rose dramatically during the 1970's and
sustained its high level in the 1980's it appeared
that gasoline produced from natural gas which would
25   economically compete with refined gasoline could be
accomplished by coupling a conventional methanol
production plant front end to a Mobil MTG process as
the finish end.

     In the early 1980's New Zealand, which then
30   depended for its gasoline supply totally on imported
crude oil products, undertook at a cost of about 1.2

billion dollars to construct a plant for production
of gasoline from methane. The overall plant design
comprised two main units, one for the production of
methanol from methane, and the second using the

5   Mobil MTG technology for converting methanol to
gasoline. In effect, the New Zealand synthetic
gasoline plant is two separate plants built side-by-
side on common grounds.   Installation of the
New Zealand plant was complete and operations

10   commenced in 1985. At that time, crude oil prices
had fallen significantly from their previous level
and synthetic gasoline produced by the New Zealand
plant was, and still is, economically uncompetitive
with the price of refined gasoline; in major reason

15   because of the cost, both capital and operating,
associated with producing methanol from methane.

In an attempt to improve the economies of
synthetic gasoline production using the Mobil MTG
process Haldor Topsoe developed a process now

20   commonly known as the Tigas process. The Tigas
process integrates methanol synthesis and gasoline
synthesis into a single process loop which
eliminates the separation of methanol as a discrete
intermediate product. To accomplish this

25   integration, Tigas combines both strains of
conventional wisdom prevailing in standard methanol
production operations in order to eliminate the need
to compress synthesis gas from a steam reformer to
the pressure required for operation of a methanol

30   plant. Accordingly, in the Tigas process, methane
is first steam reformed in part at a pressure of

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about 30 to 50 atmospheres (440 - 730 psi) to a high
CO_2 content precursor synthesis gas and the unreacted
methane content of this precursor synthesis gas is
then secondarily reformed by partial oxidation with
essentially pure oxygen to produce a still CO_2 rich
final synthesis gas having a pressure of about 28 to
48 atmospheres (410 - 700 psi). This final moderate
pressure synthesis gas is then sent to a reactor
containing a catalyst which is active for producing
both methanol and dimethyl ether from the synthesis
gas. Although this reactor operates at a somewhat
lower pressure than does a methanol only reactor,
because of its coproduction of dimethyl ether a high
conversion of methane based carbon to combined
methanol and dimethyl ether is still obtained.
Total conversion of natural gas input carbon to a
methoxy compound containing feed stream composition
upon which the Mobil MTG process can operate is
high. The methanol and dimethyl ether containing
product gas stream is then reacted over a Mobil
catalyst to convert the methoxy compounds thereof to
liquid hydrocarbon compounds which are separated
from the product gas stream and a portion of the
residual overhead gasses containing unreacted
hydrogen, carbon dioxide, methanol, ethane and
olefins are recycled back to the inlet of the
methanol/dimethyl ether reactor.

Although the Tigas design somewhat improves the
economics for synthetic gasoline production from
methane, it still requires a high capital cost steam
reforming unit to which Tigas adds a requirement for

a high capital cost oxygen plant to permit secondary
reforming. The high capital cost required for a
synthesis gas compressor is eliminated by Tigas in
favor of a high capital cost oxygen plant to obtain

5   in the tradeoff, a net reduction of capital and
operating cost, after the obtainment of the
synthesis gas, in the form of units of smaller duty
size down stream. Though an improvement, given the
current price for crude oil, the Tigas process is

10 not economically feasible for synthetic gasoline
production from methane in light of its high
attendant capital cost.

Some variations to the basic Tigas process have
been reported to further reduce the need for high

15 capital cost items. One such variation is reported
in U.S. Patent 4,481,305. In this variation, an
improvement in the economies of recycle is reported
to be obtained compared to the standard recycle
procedure described by U.S. Patent 3,894,102 to be

20 used with the Mobil MTG process. The improvement
requires that adjustments be made to the composition
of the synthesis gas feed to a methanol/dimethyl
ether production reactor such that the synthesis gas
feed will contain carbon monoxide and hydrogen in a

25 CO/H_2 ratio of above 1 and contain carbon monoxide
and carbon dioxide in a CO/CO_2 ratio of from 5 to 20.
A synthesis gas of such composition may be
obtainable from coal or a similar carbonaceous
starting material. It is, however, not economically

30 feasible to prepare a synthesis gas of such
composition from methane using the Tigas process.

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Even though synthetic gasoline production
processes such as Fischer-Tropsch synthesis (FTS),
standard Mobil and/or Tigas have undergone steady
improvements intended to render them more economical
5   to the production of synthetic gasoline from
methane, they are today still unable to produce
gasoline at a cost competitive to that refined from
petroleum crude. This is so even where a source of
low cost methane is conveniently located to or
10   transportable to the synthetic gasoline production
plant site.

Application of a currently existing process for
conversion of remotely located natural gas to
methanol and/or for synthetic gasoline production
15   from natural gas is not economically feasible in
view of the great capital cost associated with the
equipment necessary to practice such processes.

In commonly owned copending U.S. Patent
Application Serial No. 508,928, a process is
20   disclosed for converting natural gas to a synthesis
gas using a low grade oxygen source, i.e.,
containing 50% or more nitrogen, which significantly
lowers the capital cost of a methane to methanol,
dimethyl ether or gasoline production plant. In one
25   embodiment of the disclosed invention a gas turbine
is utilized to power the compressors needed to
compress methane and air in the process steps of the
methane to synthesis gas conversion. In addition,
the gas turbine provides a ready supply of
30   compressed air in the range of about 8 to 16
atmospheres absolute. Compressed air from the

turbine is bled off in an amount not exceeding the
mass balance requirements of the turbine. The so
compressed gas is then compressed in a secondary
compressor, which may be powered by the energy
5   output of the gas turbine, to the required 400 to
2000 psig oxygen gas compression requirement of the
process. Thus, a primary compression of the oxygen
containing gas of from about 8 to about 16 fold
produced by the turbine is achieved at little or no
10   cost. The remaining 1.8 to 17 fold compression
required of the secondary compressor can be achieved
at considerable savings over the 28 to 137 fold
compression which in the absence of the gas turbine
would be performed on the oxygen containing gas by
15   conventional gas compressor units.

As further described in copending U.S. Serial
No. 508,928, the economics and efficiencies of the
process of converting natural gas to a recoverable
normally liquid hydrocarbon can be further improved
20   by preparing the synthesis gas with an oxygen
enriched gas having up to 50 mole % oxygen.

Such oxygen-rich gas normally contains nitrogen
as its other main component. Presently there are
three different ways to arrive at such a gas,
25   normally described as oxygen-enriched air.

Smaller amounts of such gas are made by
preferential diffusion of oxygen over that of
nitrogen through an appropriate membrane. In order
to drive that diffusion, air is compressed and then
30   fed to the diffusor unit. This diffusor unit can
employ flat membranes, but it is often preferred to

use a large number of small hollow membrane fibers. Either the compressed air is fed to the inside or to the outside of the membrane fibers. When fed to the inside, the fiber can be thin-walled. This helps

5 the diffusion, but limits the maximum pressure to about 150 psig. It is also possible to feed the compressed air to the outside of the fibers. Then the wall of these fibers has to be thick enough to withstand the pressure. This leads to the use of

10 higher pressures, but the greater wall thickness slows the rate of diffusion down. It should be clear, that the air compression is a cost factor, but higher compression within the limits of tolerance speeds up the diffusion, thus lowering the

15 cost of the fiber material. In practice optimization of these two effects has led to compression of air to 8 atmosphere gage (atg), followed by a rather intensive use of the amount of air. The residual gas, or "spent air" commonly

20 contains little more than 7 % oxygen. The cost of the air compression, both in capital and in operation, is substantial. The cost of the membrane fiber material, together with a containment vessel therefor and the necessary air filters, is mostly

25 capital only. Enriched air made this way has a very high oxygen equivalent cost, well over $50 per metric ton. The term "oxygen equivalent cost" derives from the assumption that the same amount of enriched air can also be made by adding pure oxygen

30 to air. When assuming air to have no cost, the cost of the enriched air is the cost of that amount of

pure oxygen which must be added to produce an
equivalent volume.

While a membrane diffusion method is commonly
used for preparation of small amounts of such
5   enriched air, larger quantities may be produced by
pressure swing absorption (PSA). Here compressed
air is contacted with an absorbent that
preferentially absorbs oxygen. As soon as the
absorbent is saturated to a reasonable degree with
10   oxygen, the flow of the pressurized air is stopped
and the pressure reduced to atmospheric and oxygen
is desorbed. Thus mainly oxygen is produced, be it
at low pressure. The term pressure swing derives
from the alternating of pressurized absorption and
15   low pressure desorption.

The cost of oxygen made by PSA, is much lower
than with diffusion. However, the PSA cost is still
substantial. For still larger amounts of oxygen,
say 500 metric tons per day (MTPD) and higher,
20   cryogenic separation of oxygen is the preferred
method. Then the cost of oxygen at present can be
brought down to the zone of $25 to a $35 per metric
ton.

Hegarty U.S. Patent No. 4,545,787
25   describes a process wherein an oxygen enriched gas
may be prepared at low utility cost -- for the
volume produced -- by the incorporation of an oxygen
permeable membrane separation unit or PSA with the
operation of a gas turbine operated for power
30   generation. Unfortunately, in view of the mass and
thermal balance tolerance constraints which must be

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observed for proper operation of the gas turbine,
the process described by Hegarty only provides for
the separation of a minor amount of oxygen from a
portion of the compressed air provided by the
5   turbine.

Feeding air at 11 atmospheres absolute (atà) to
a membrane with a gas separation factor for O_2 versus
N_2 of 5.55 can provide a permeate stream of about 54%
O_2 in a volume amount of about 1.5% of the volume of
10   feed air. The same membrane can produce a 49 mole%
O_2 permeate in a volume amount of about 17.6% of the
volume of the feed air, or a 40 mole% O_2 permeate of
about 40.5% of the volume of the feed air. In the
last case the remaining O_2 in the used air amounts to
15   only 8% . In each case the balance of the O_2
enriched permeate gas is comprised essentially of N_2.
Theoretically, if all O_2 of the feed air is extracted
into the permeate the permeate will be about 35
mole % O_2 and be of a volume of about 50% that of the
20   feed air.

Hegarty U.S. Patent 4,545,787 proposes to
compensate for the disruption to the thermal balance
between the compressor and expander side of a gas
turbine which is caused by the recovery of O_2 from
25   the compressed air by increasing the amount of air
compressed by the compressor side in a quantity
equal to the amount of O_2 diverted into the permeate
O_2 enriched gas stream. Hegarty proposed that this
maintains the same molar flow to the expander side
30   as would be the case had no O_2 been recovered.

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Turbines are designed to pass all air compressed in the compressor side to the expander side. In normal operation the only mass imbalance between compressor to expander side is due to the mass increase caused in the expander side by reason of fuel supplied to the combustion chamber of the expander side. The turbine design provides for this positive mass imbalance and further for a safety factor of a positive mass imbalance preferably no greater than a 10% increase of mass in the expander side. The operation of a turbine in a manner which exceeds the positive mass imbalance safety limit, or which produces a negative imbalance by decreasing mass flow in the expander side, will result in a significant lessening of its service life and even to its total failure.

Even were one able to put Hegarty's proposal to practice, for the same amount of fuel input to cause the compressor side of the turbine to compress additional quantities of air equal in an O_2 amount to the O_2 recovered, Hegarty's method would not maintain the turbine in a tolerable mass balance even if the requirement of thermal balance were met. Hegarty simply does not address nor consider the problem of proper mass balance.

For example, with a membrane having a gas separation factor for O_2 of 5.55 employed in Hegarty's method with a turbine compressing 1000 lb.-mole/hr air (21% O_2, 79% N_2) which is 314% of that amount required for fuel combustion (33.44 lb.-mole/hr CH_4), without Hegarty's proposed additional

air compression the mass imbalance of the turbine would be negative and would exceed 10% when the O_2 recovery reaches or exceeds about 64.3 lb-mole/hr O_2 since the permeate would also contain about 48.7 lb-mole/hr N_2. Following Hegarty's proposal to compress an additional quantity of air equal to the extracted O_2 would produce a negative mass imbalance of 16%; compression of an additional quantity of air equal to the sum of the O_2 and N_2 lost in the permeate would produce a negative mass imbalance of 19.5%.

It is evident that one of two realities will quickly become apparent to one who attempts to practice the process of Hegarty, namely that either the quantity of O_2 produced must be limited to a small quantity to prevent an intolerable mass imbalance or the turbine must be sacrificed to a short service life or even failure.

Accordingly, even in view of Hegarty's proposal, the fact remains the same today that membrane O_2 enrichment is economically viable only for production of small quantities of O_2; for medium volume amounts of produced O_2 a pressure-swing absorption method of O_2 production is viable and wherein large quantities of O_2 are required an efficient but capitally intensive cryogenic method for O_2 production is still the most economically viable process for production of such large quantities.

There is still a need for a method of production of useful O_2 in large volumes at a production cost significantly less than that

available by conventional methods. Such a method
would allow the use of an oxygen enriched gas for
the improvement of many industrial scale processes
to provide valuable products at significantly
5   reduced production cost.

SUMMARY OF THE INVENTION

This invention comprises a process and
apparatus for the production of a gas mixture of
10   oxygen and nitrogen which, in comparison to air, is
enriched in oxygen. The degree of oxygen enrichment
obtained, considered on the basis of the amount of
pure oxygen which would be required to be added to a
quantity of air to provide a gas mixture of similar
15   volume and of equivalent mole % oxygen, is obtained
at a significantly reduced cost than that which
could be provided by conventional methods of oxygen
generation.   The invention comprises a technique
for separating air into an oxygen-rich gas stream
20   and an oxygen-poor gas stream, using a gas turbine
to provide pressurized air as feed to the device
that separates the pressurized air into the two
desired streams.

Two types of oxygen enrichment units can be
25   used to achieve the desired separation, namely
pressure swing absorption (PSA) and diffusion
through a membrane, which preferentially passes
oxygen through over nitrogen.

Especially when using a diffusion unit, the
30   oxygen enriched gas stream obtained will contain
appreciable amounts of nitrogen. It is part of the

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invention to show how such oxygen enriched gas,
containing at least 40 % nitrogen, is useful for
processes in general. It will be shown how such
oxygen enriched gas may be utilized to produce a raw

5   synthesis gas can be utilized for the production of
a number of marketable products, like methanol,
gasoline, kerosene, diesel, ammonia, and others.
Further described is how the integration of the
production of oxygen-rich gas with the different

10   processes can lead to an attractive use of the final
bleed stream out of such processes as fuel for the
gas turbine which provides the pressurized air for
the production of the oxygen-rich gas stream.
       The reason for the lower cost of the oxygen

15   enriched air produced by this invention is that the
pressurized air, produced in the compressor unit of
the gas turbine, is only partly necessary for
combustion of the turbine fuel. The rest of the
air, which is used for cooling, can be used as feed

20   for the diffusor device at no extra cost. It can be
available at a substantially higher pressure than in
standard diffusor unit, where economic
considerations decide the compression ratio.
Finally, it is not necessary to diffuse out as much

25   oxygen as possible, as sufficient compressed air
generally is available. The final oxygen
concentration in the spent air is generally
substantially higher than in a stand-alone diffusor
unit. The gas, diffusing through the semipermeable

30   membrane, contains at least 40% nitrogen. This gas

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may be immediately reduced in oxygen content by
mixing with air, fed in for this purpose.

The diffused gas, or the gas obtained from it
by mixing with air, may be utilized to reform
5   carbonaceous starting materials like natural gas,
naphtha, heavy oil, and solid carbonaceous materials
like coal, by adiabatic reaction to a raw synthesis
gas containing at least H_2, CO, and a substantial
quantity of N_2. Many carbonaceous starting materials
10   are available for the use of this invention.
Without eliminating the possible use of this
invention to heavier starting materials, the use of
low-cost natural gas, such as remote natural gas, is
the most attractive. The N_2 containing raw synthesis
15   gas may be modified to adjust its compositional
makeup to that which is most suited to its
conversion to final marketable products, such as
methanol, gasoline and diesel grade normally liquid
hydrocarbon, ammonia, and others. The vent or tail
20   gas remaining after the product taking operation
comprises some unreacted H_2, and/or some CH_4; in
many cases the tail gas also contains CO, but that
depends on reaction conditions. Other hydrocarbons
than methane may also be present. The vent or tail
25   gas is utilized as fuel gas for powering a gas
turbine which in turn supplies the
power/energy/driving requirements for production of
the oxygen enriched gas stream and other process
requirements for synthesis gas production and
30   conversion thereof into final products.

The integration of the gas turbine with an oxygen enrichment unit for the production of a raw synthesis gas which is then processed to final products requires that careful consideration be

5 given to means within the overall processing scheme for complying with the mass and thermal balance tolerances required for proper gas turbine operation. This invention provides means for complying with the mass and thermal requirements of

10 the gas turbine even though the volume of oxygen enriched gas separated from the compressed air provided by the turbine and hence diverted from the operation of the turbine is greatly in excess of that which has heretofore been possible when

15 considering the mass and thermal balance requirements needed for operation of a turbine in its normal mode.

Further, depending upon which final product one desires to produce from the raw synthesis gas, the

20 processing methodology applied to a conventionally produced synthesis gas, from which significant quantities of N_2 are absent, is modified in various respects, as will be explained, by reason of the presence of significant amounts of N_2 in the raw

25 synthesis gases produced in accordance with this invention.

In broad overview, this invention comprises a method and apparatus for the production of oxygen enriched air -- i.e. an oxygen containing gas having

30 at least 40 mole % nitrogen -- which provides low cost oxygen in large volumes. The apparatus

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comprises a gas turbine in integration with an
oxygen separation unit, preferably a diffusion
membrane unit, and means for complying with the mass
and thermal balance tolerance requirements for
5   proper and safe operation of the gas turbine. The
low cost oxygen so produced may be utilized to
increase the efficiency of other process operations
which require oxygen, such as a combustion operation
for the generation of electrical energy or the Claus
10   Process. Preferably the low cost oxygen is utilized
in the reforming of a carbon source, such as natural
gas, by adiabatic reaction to a raw synthesis gas.
The raw synthesis gas is preferably processed to a
normally liquid hydrocarbon such as; methanol by
15   reaction over a methanol catalyst; or methanol and
dimethyl ether (DME) over a methanol/DME catalyst
which in turn is reacted over a Mobil catalyst to
produce normally liquid hydrocarbon products; or to
gasoline/diesel grade hydrocarbons by reaction under
20   Fischer-Tropsch Synthesis (FTS) conditions.
Alternatively, since the raw synthesis gas produced
by this process is of a high N_2 content it may be
utilized for the production of ammonia by reaction
over a ruthenium-based catalyst. However processed,
25   the tail gas remaining following the last take of
product compounds is preferably utilized as fuel gas
for the gas turbine.
        The method of this invention eliminates the
need for steam reforming and/or adiabatic reforming
30   with essentially pure oxygen of the natural gas to a
synthesis gas. In accordance with the process of

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this invention, a synthesis gas may be produced at
an operating pressure suitable for conversion
thereof to methanol and/or dimethyl ether with
little or no need for synthesis gas recompression.

5   Further, processing conditions are so chosen that
the vent or tail gas from the overheads after
conversion to the crude product methanol/DME and/or
its conversion to gasoline grade liquid
hydrocarbons, generally has a BTU value required to

10 serve as a fuel gas for supplying the energy needed
for operation of the gas compression equipment
requirements by which the process of this invention
may be practiced. In some cases a small amount of
natural gas may be added to the final tail gas to

15 increase its fuel value. Accordingly, the capital
and operating cost associated with the production of
methanol, DME and gasoline from natural gas by a
Mobil MTG process is significantly reduced by the
method of this invention and renders it economically

20 feasible for natural gas recovery processing at
remote locations.

        Further, the process and apparatus of this
invention may be utilized for the production of a
synthesis gas which is reacted under Fischer-Tropsch

25 Synthesis conditions to a hydrocarbon mixture
containing appreciable quantities of waxy materials;
these waxy materials can be hydrofined to a high
quality diesel fuel of normally liquid composition.
The utilization of the process and apparatus of this

30 invention requires a modification of the standard
scheme of the Fischer-Tropsch processing to

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accommodate the FTS to operation on the synthesis
gas of the present invention which contain
appreciable amounts of nitrogen.

      An oxygen enriched gas is obtainable at low

5   costs from compressed air from the compressor of the
gas turbine employed in the process to power the
compressor and heat exchangers required. Air
compressed from about 8 to about 16 atmospheres
absolute is withdrawn from the high pressure side of

10   the gas turbine compressor and passed through an
oxygen separation unit which is preferably a semi-
permeable membrane that is selective to oxygen over
nitrogen. Contacting the compressed air with the
membrane yields a low pressure oxygen enriched

15   permeate gas stream and a high pressure oxygen
depleted non-permeate gas stream. The oxygen
depleted gas stream is returned to the combustion
unit of the turbine to partially restore the mass
balance through the energy production unit turbine.

20   The produced oxygen enriched gas stream is available
for use in other process steps of the invention.
The semi-permeable membrane which may be employed in
the invention may produce an oxygen enrichment in
excess of 35 mole %. When the oxygen enriched gas

25   requires recompression for its subsequent
utilization, it is preferred to utilize it at 35
mole % O_2 or less in order to avoid the need for
compressors of special construction. Accordingly,
when the membrane process is operated to produce a

30   permeate gas enriched to greater than 35 mole % O_2,
provision is made to dilute the permeate gas with

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air to obtain an oxygen enriched gas stream of 35
mole % O_2 or less. Preferably, this dilution is
performed at the membrane surface by passing a
continuous air stream over the oxygen enriched or
permeate side of the membrane. In this manner, two
purposes are served, the first being the preferred
dilution to an oxygen content of about 35 mole % O_2
or less. The second purpose is to maximize the O_2
partial pressure gradient across the diffusor
membrane, thereby providing a maximum throughput of
oxygen through the diffusion unit, albeit oxygen in
the resulting gas stream is in more dilute form than
otherwise obtainable.

To further maximize the oxygen transported
across the membrane, the diverted compressed air
from the turbine compressor may be further
compressed above the compression performed by the
gas turbine compressor. The steeper pressure
gradient across the membrane increases the overall
rate of oxygen throughput of the system.

In a primary embodiment of this invention the
oxygen enriched gas is passed to an adiabatic
reactor to which natural gas is supplied and the
natural gas there reacts with a quantity of an
oxygen enriched gas containing greater than 21 mole
percent oxygen and at least 40 mole percent nitrogen
such that, upon the completion of the reaction, a
raw synthesis is produced having a temperature
between 1800 and 2500 °F and at least about 90 mole
percent of the natural gas hydrocarbon carbon
content is converted to carbon monoxide and carbon

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dioxide and about 1 to about 10 mole percent of such
natural gas hydrocarbon carbon components are
present in the reformed gas as methane.   This
raw synthesis gas may then be treated in various
5   ways to particularly accommodate it to various
processes by which its H_2, CO, and N_2 content may be
made to undergo reaction to form different products,
such as methanol, dimethylether, synthetic gasoline,
synthetic diesel fuel, ammonia, etc. For instance,
10   for methanol or methanol to gasoline processing, the
raw synthesis gas is dewatered and thereafter
processed according to the methods disclosed in
commonly owned copending U.S. Patent Application
Serial No. 508,928. For processing by Fischer-
15   Tropsch reaction the raw synthesis gas is first
subjected to a degree of a water-gas shift reaction
to adjust its H_2:CO ratio to that most preferred for
the Fischer-Tropsch reaction. This is followed by
CO_2 removal at some point in the process. However
20   the raw synthesis gas is modified, by reason of its
substantial nitrogen content, certain modifications
need to be made to the processes in which it is
subsequently used.

       The use of an oxygen enriched gas results in
25   process efficiencies over a process which uses air
as disclosed by commonly owned U.S. Patent
Application Serial No. 508,928. More complete
reaction is obtained in the adiabatic reforming
stage of the process and at the same time less
30   additional work is performed to compress the lesser
amount of nitrogen present in the synthesis gas

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during its utilization in subsequent process
operations.   To prepare the raw synthesis gas to
be of a composition most suitable for methanol
production the raw synthesis gas is cooled to
5   condense H_2O and H_2O is removed from it.   The
presence of a substantial mole percent of inert N_2 in
the synthesis gas composition has, surprisingly,
been found not to greatly affect a need to increase
the pressure required to convert the carbon monoxide
10   and hydrogen components therein to methoxy
compounds, particularly methanol and DME compounds,
by contact with catalyst compositions typically
employed to affect such conversion with a synthesis
gas having a low N_2 content as prepared by steam
15   reforming, adiabatic reforming with essentially pure
O_2 or a combination thereof. When making only
methanol, the absence of need to greatly increase
the pressure follows from the decision to accept a
slightly lower conversion of carbon to a methoxy
20   containing product compound. The negative effect of
this lower conversion combined with the low cost of
remotely located natural gas is more than outweighed
by the lower capital cost resulting from the use of
a high nitrogen content oxygen enriched gas to form
25   the synthesis gas which eliminates the need to
prepare the synthesis gas by steam reforming or
adiabatic reforming with essentially pure oxygen.
Further the need to compress the synthesis gas to a
pressure necessary for conversion to methanol with
30   standard methanol catalysts may be significantly
reduced or even totally eliminated. This

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significantly reduces or eliminates the capital
equipment costs associated with the need in standard
methanol production methods for compressing the
synthesis gas prepared by steam reforming or
5   adiabatic reforming with essentially pure oxygen to
the pressure needed for conversion to methanol.
Beneficially, the high nitrogen content of the
synthesis gas allows plug flow conversion to
methanol in two or three reactors in series, thus
10   eliminating the costly recycle routinely practiced
in conventional methods for methanol production.
        For the case of combined methanol-DME
manufacture, the preferred pressure range is similar
to that of the standard methanol process,
15   notwithstanding the large N_2 content of this
synthesis gas. This is especially the case when
first methanol is prepared and separated in one or
two steps before contact of the remaining synthesis
gas with a methanol-DME catalyst to prepare a
20   methanol-DME mixture. The advantage of being able
to use plug flow reactors also applies in this case
and is important.
        Accordingly, this discovery permits production
of methanol and/or DME from natural gas using
25   standard methanol/DME catalyst compositions and
conversion technology but without the need for
employing a high capital cost steam reformer or a
high capital cost oxygen plant as are required in
methanol conversion units of conventional design,
30   and this without greatly increasing the capital cost
of the rest of the process facility.

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As an alternative to conversion to methanol
only or the production of gasoline by a Mobil MTG
process, the raw synthesis gas produced by this
process can be conditioned for use by Fischer-
5   Tropsch processing into high grade diesel fuel. For
this application the raw synthesis gas is partially
water gas shifted to react a portion of its CO
content with its water content to provide a gas
composition wherein the ratio of H_2:CO is from about
10   1:1 to about 3:1 preferably about 2.02:1 to about
2.4:1. Following the water gas shift, the resulting
gas mixture is preferably first contacted with a
medium which extracts CO_2 therefrom to yield a gas
mixture in which CO_2 is present in a quantity of 1
15   mole % or less and this gas mixture is then reacted
under conditions and over a catalyst that promotes.
the Fischer-Tropsch reaction between H_2 and CO to
form a hydrocarbon mixture, ranging in composition
from a low to high carbon number, finally being in
20   the paraffin to waxy range, and the hydrocarbons
formed are condensed by cooling. The balance of the
gas is then mixed with the earlier recovered CO_2 and
subjected to a reforming reaction under heat input.
Heat may be provided by the hot gas stream made by
25   the adiabatic reaction. The gas stream resulting
from this second reforming step is enriched in
hydrogen. CO_2 is removed, and a second Fischer-
Tropsch step is taken, likewise resulting in a
partial waxy product. The recovered hydrocarbons
30   from the first Fischer-Tropsch step are added back
in and the combined stream is subjected to

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hydrocracking conditions wherein the remaining H_2
content of the gas stream reacts with the
paraffinic/waxy hydrocarbon portions to convert it
to a normally liquid hydrocarbon compound in the
5   carbon number range of diesel fuel. It is also
possible at a limited loss in yield to eliminate the
first CO_2 removal step. The tail gas from the
hydrocracking unit is then returned to the gas
turbine as fuel.

10   Whether the process of this invention is
utilized solely for crude methanol production, or
whether it is used in combination with a Mobil MTG
unit for production of gasoline, or whether it is
used in a Fischer-Tropsch process for production of

15   diesel grade fuels the final overhead gas from the
finish end of this process contains a sufficient BTU
content to be utilized to supply most, all or in
excess of the fuel BTU/scf gas energy required for
operation of the gas turbine for production of

20   operational power and for equipment operation needed
in the practice of this process.

        In addition, when the raw synthesis gas is
utilized for the production of a hydrocarbon
containing product compound, the overhead gas

25   contains all of the nitrogen which was initially
diverted from the compressor unit away from the
energy production unit of the gas turbine as a
component of the oxygen enriched gas stream. This
nitrogen is returned to the energy production unit

30   of the turbine in the final overhead gas fuel
therefor and is present to aid in the proper

preservation of the mass balance of the gas turbine
power plant. Accordingly, the return of this N_2 with
the tail gas as fuel for the turbine allows for a
greater volume production of the O_2 enriched gas

5   stream in the first instance. The inert nitrogen
content of the fuel produces a like cooling effect
in the energy production unit as the compressed air
from the unit. Thus, the thermal balance
requirement, a feature of all gas turbines, is

10 restored to near that which would occur if none of
the oxygen and nitrogen of the turbine compressed
air stream were withdrawn from the turbine for use
in downstream units of the overall process.

One aspect of the gas turbine operation cannot
15 be overlooked. The present invention proposes to
monitor the final temperature of the cooled flame
effluent, the so called turbine inlet temperature
(TIT), closely. Assuming that to be unchanged from
a standard operation, it is also self-evident that

20 the nitrogen dilution of the fuel leads to a lower
flame temperature. In most gas turbines sufficient
volume is provided for the formation of the flame
and the after-oxidation expansion of the oxidized
primary product so that dilution of the fuel with

25 nitrogen can be tolerated. In cases where the
dilution is large and the gas turbine has a
relatively small volume for formation of the flame;
it would be necessary to provide a larger flame
volume. This is possible at very limited cost in

30 those gas turbines which have outside combustion
unit. Then it is easy to provide a somewhat larger

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fuel chamber to counteract the lower flame
temperature. When the fuel chamber is very limited
by the geometry of the design, nitrogen dilution may
be limited.

5   In those embodiments of the process which
utilize a quality of air as a diluent or stripper
air to flow across the permeate side of the oxygen
diffusion membrane unit, control of the quantity of
stripper air supplied provides a means for

10   maintaining the thermal and mass balance
requirements of the turbine within the tolerance
constraints required for proper turbine operation.
In this circumstance, since all of the nitrogen
initially diverted from the energy production unit

15   of the turbine by reason of its diffusion into the
enriched oxygen stream is ultimately returned to the
energy production unit in the tail gas fuel, the
difference in mass and thermal balance between
compressor and energy production units of the

20   turbine compared to normal turbine operation is
represented by that amount of diverted O_2 which is
consumed by chemical reaction and diversion out of
the overall process loop as separated water or in
methoxy type products. Accordingly, the quantity of

25   stripper air may be regulated as a means to make up
for this deficiency by supplying a quantity of N_2 in
an amount necessary to bring the mass and thermal
balance of the gas turbine back within tolerance
limits.

30   In those embodiments of the process wherein the
N_2 content of the oxygen enriched gas is not entirely

returned to the gas turbine in the fuel supply
therefor, such as wherein the N_2 in the raw synthesis
gas is utilized as a reactant, and hence the amount
of N_2 returned to the energy production unit in the

5 tail gas fuel is reduced, such as in utilization of
the synthesis gas for production of ammonia; or in
those embodiments wherein of the oxygen gas is
utilized for increasing the throughput capacity of a
Claus unit; low pressure steam can be added to the

10 gas fuel for the turbine to make up the N_2 deficiency
and by this means the thermal and mass balance of
the turbine is maintained within tolerance. Such
low pressure steam is invariably available in an
ammonia or Claus production process.

15   At times the BTU content of the final overhead
gas may exceed all of the compression and heat
exchange requirements for the process and excess
power can be produced for export from the process,
for instance in the form of electricity. In that

20 case, other excess heat in the process can be used
to generate steam and thus provide more power for
electricity generation.

     In the most preferred embodiments of the
process, the final vent or tail gas from the finish

25 end of the process is recycled as fuel to the
energy production unit of the gas turbine, wherein
by complete combustion with compressed air, driving
energy requirements are supplied for at least a
first step of compression of the oxygen enriched gas

30 used in this process and also for the operation of
the gas compressors by which the natural gas stream

and the oxygen enriched gas are compressed to the
final pressures desired for the reaction
therebetween which provides the carbon monoxide and
hydrogen containing raw synthesis gas.

5

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 schematically illustrates a gas
turbine.

Figure 2 schematically illustrates a unit

10   design wherein a gas turbine supplies compressed air
to an air separation unit for the production of a
gas stream enriched in oxygen to a level greater
than 21 mole% O_2 and having at least about 40 mole %
N_2. This oxygen enriched stream is preferably used

15   to improve the efficiencies of an oxidization
dependent process which produces a final overhead
gas stream containing unreacted H_2, methane, possibly
higher hydrocarbons, and possibly also CO, together
with appreciable amounts of N_2 which are returned to

20   and utilized as a fuel gas and mass balance for the
gas turbine.

Figure 3 schematically illustrates a unit
design where the gas turbine is utilized to operate
gas compressors by which an oxygen enriched gas

25   stream as produced in Figure 1 and a natural gas
stream are compressed to the pressure required for
adiabatic reaction to form a raw synthesis gas, the
raw synthesis gas is then processed to recoverable
products to leave a final overhead gas stream

30   containing some reacted H_2, CH_4 or other hydrocarbons

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and N_2 which is returned to the gas turbine as fuel and mass balance.

Figure 4 schematically illustrates a unit design wherein a nitrogen containing synthesis gas as produced by the unit of Figure 2 may be processed by a Fischer-Tropsch technique to a waxy hydrocarbon intermediate product which may then be hydrofined to a high grade diesel fuel liquid hydrocarbon product. A final overhead gas stream containing methane and N_2 is returned to the gas turbine as fuel and mass balance.   In the different figures like parts are identically numbered.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

This invention comprises a method and apparatus for obtaining from air an oxygen enriched gas mixture containing at least 40 mole % nitrogen. The apparatus comprises a gas turbine, an oxygen separation unit which is in fluid communication with the turbine air compressor and means for maintaining a proper mass balance tolerance between the turbine compressor/unit and the turbine energy production unit. The method comprises supplying compressed air from the outlet of a compressor unit of a gas turbine to an oxygen separation unit, preferably to a membrane diffusion unit, wherein by preferential separation the gas components become separated into a lower pressure oxygen enriched permeate gas having at least 40 mole % of N_2 and to a high pressure oxygen depleted non-permeate gas which is provided to an energy production unit of the gas turbine,

method means for matching the mass balance between the compressor and energy production units of the gas turbine to comply with a tolerance for mass imbalance of the turbine as determined by a thrust bearing of the turbine, and method means for obtaining the thermal balance required in the energy production unit of the turbine.

The Gas Turbine

Basically, a fuel turbine comprises an air compressor unit and an energy production unit. With reference to Figure 1, the energy production unit comprises a combustor unit 26 in which a fuel supplied by line 28 is completely oxidized to provide a combustion gas, a first expander unit 32 through which the combustion gases are first expanded to provide the energy needed to drive the air compressor unit 8 by a shaft 34 carrying a thrust bearing 36 between the first expander unit and the air compressor unit, and a further secondary expander unit 38 through which the combustion gases which were first expanded in the combustor expander unit 32 are further expanded to provide a driving force which, by mechanical linkage 42 to the secondary expander unit 38, can operate other items of equipment such as compressors, electrical generators, and the like, as denoted by units 44 and 46.

Turbine designs initially evolved as a power source for powering jet aircraft, wherein the gases exhausted through the secondary expander unit 38 of

the energy production unit provided the motive force
to propel an aircraft. As designed for aircraft
propulsion a turbine operates on a liquid
hydrocarbon fuel source wherein the oxidization gas
source -- air -- is compressed by the compressor
unit in an amount which, is 4:1 in older aircraft
turbine designs, and 3:1 in more recent aircraft
turbine designs, that of the stoichiometric amount
of O_2 needed to completely oxidize the turbine fuel
source.

Aircraft turbine designs contemplate that all
air compressed by the compressor unit 8 thereof is
fed to the energy production unit, in various
proportion to the combustor unit itself as by line
16 and 18 and the remainder to the combustion gases
as a gas temperature control fluid, as, for example
by lines 20, 22 and 24. In turbines of an aircraft
design there exists an inherent mass imbalance
between the air compression unit of the turbine and
the mass total which flows through the energy
production unit. This imbalance resides in the fact
that an additional quantity of mass must be supplied
to the energy production unit as fuel, per line 28.
Accordingly, the design of a turbine for aircraft
production accounts for this mass imbalance in the
design of the turbine itself.

On the shaft 34, coupling the air compressor
unit 8 to the first expander 32 of the energy
production unit, a thrust bearing 36 is placed,
which allows for up to a 10% increase in the mass
fed to the energy production unit over that fed to

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the air compressor unit. This bearing is necessary,
because addition of the fuel increases the mass flow
through the energy production unit, which increase
will vary with the mass variation in the fuel flow.
5   With aviation fuel or pure methane the mass increase
is less than about 2%, but with poorer fuels the
mass of fuel for the same total heating value can
increase substantially. The 10% value is sufficient
for standard operation of a turbine.
10   After the design of turbines for aircraft
propulsion had been resolved, other non-aircraft
uses of such turbines were devised. In uses such as
the motive means for generation of electrical energy
or operation of other items of equipment a
15   carbonaceous fuel other than an aviation grade
liquid hydrocarbon may be, and preferably is, used.
Such other fuel sources contemplate natural gas,
i.e., methane, as a fuel for the turbine, and it is
such a turbine which herein is referred to as a "gas
20   turbine." That is, any turbine which operates with
a normally gaseous source of a carbon based
oxidatable fuel is hereinafter referred to as a "gas
turbine." Such gaseous fuel source may be a high
grade BTU/SCF gas, like methane, ethane, propane,
25   butane, or analogous unsaturated hydrocarbon
compounds or mixtures thereof, or other carbon
containing compositions. Also, within the context
of the invention herein described, the fuel source
of such gas turbine may be a lower BTU/SCF gaseous
30   source which contains, for example a significant
content of oxidizable inert normally gaseous

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compounds, such as N_2, CO_2, or water vapor (steam),
in conjunction with oxidizable compounds, such as H_2,
CO, a hydrocarbon whether saturated or unsaturated
and whether or not a hydrocarbon derivative such as
5   methanol and/or dimethylethyl or other oxidizable
carbon compound based compound.

In any event, a turbine if of conventional
design for aircraft propulsion -- whether operated
on a normally liquid hydrocarbon fuel or on a
10   normally gaseous carbon based fuel source, is
typically designed with a thrust bearing 36 capable
of a maximum tolerance of a 10% increase in mass in
the energy production unit over that mass of air fed
to the air compressor unit. This design constraint
15   dictates the directional positioning of the thrust
bearing by which this design tolerance is
maintained.

The thrust bearing 36 of a turbine of such
design does not protect against a lower mass flow to
20   the energy production unit. If that is expected, a
reverse thrust bearing of the right capacity should
be placed on the shaft connecting the air compressor
with the first expander of the energy production
unit.

25   It is important to note that the gas turbine
has several operational requirements. In the first
place the flame generated in the combustion unit 26
has to substantially convert all the fuel into
combusted products. In the conventional design of
30   the combustor unit 26 a substantial latitude is
normally built in. In other words the manufacturer

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of the gas turbine has allowed for burning of both
better and poorer quality fuels. Of course this is
within certain reasonable limits. If the fuel
becomes very poor, the burner volume will not be
5   sufficient. Burning is governed by partial
pressures of fuel and oxygen, together with
temperature. At low oxygen partial pressure and low
temperature the given volume of the burner may not
be sufficient. It is therefore important for this
10   invention, in which low quality fuels may be used,
to have the possibility for increasing the volume of
the burner. This is relatively easy with turbines
of an outside burner chamber design and much more
difficult, if not impossible, for gas turbine
15   designed with combustion units which are built into
or practically built into the first expander sector.

A very important further point in the operation
of the gas turbine is that the temperature of the
20   gases exiting the combustor unit has to be
controlled closely to the design temperature. A
lower temperature obviously results in loss of
energy provided. A higher temperature than the
design seriously reduces the service life of the
25   turbine. Temperature control is effected by
continuous determination of the heat of combustion
of the fuel and control of the amount of air and
fuel, together with temperature of both.
In standard gas turbine operation, the turbine
30   inlet temperature (TIT) is kept close to the maximum
permissible TIT set by the turbine design by

monitoring the heating value of the fuel. Slight
changes in that heating value are compensated by
small variations in fuel flow.

In this invention the amount and heating value
5   of the tail gas stream out of the process are both
monitored. The inlet temperatures of all gas
streams to the combustor unit are adjusted to obtain
a TIT within 200°F of and not exceeding the maximum
permissible TIT of the turbine design.

10   As already stated, the normal design of a gas
turbine does allow for up to a 10% increase in mass
between the compressor unit and the energy
production unit. When gases are taken out of the
compressor unit and/or highly diluted fuels are
15   used, one may either obtain a reverse thrust, due to
a lower mass flow to the energy production unit in
the first case, or a higher than 10% mass flow
difference in the case of highly diluted fuel. This
last case is important when tail gases are used of
20   low BTU content are used as fuel for the turbine.
Proper thrust bearing changes have to be made to
accommodate these changes.

When utilizing a turbine of typical design for
production of an O_2 enriched gas stream, the limits
25   on the amount of the O_2 enriched gas stream which can
be produced are governed by the positive thrust
bearing tolerance of 10%. One means for increasing
this limiting factor is to replace the typical
thrust bearing 36 with one designed for a greater
30   positive mass imbalance than 10%.

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  Finally, especially when using tail gas streams
processes as fuel for the turbine, as will be
discussed with reference to Figure 2, the task of
the combustor unit 26 has to be examined closely.

5 The standard design of gas turbines allows use of
fuels of lower heating values than standard natural
·gas. Heating values of 100 to 300 BUT per SCF are
considered acceptable in some, if not all gas
turbines. Still lower values definitely would call

10 for larger combustion chambers. This necessity
derives from the fact that given a total unchanged
mass flow and a final constant temperature in the
exit of the combustor unit, the flame temperature is
lowered when a larger part of the total mass is

15 directly fed into the flame. Also, that extra mass
dilutes the reacting species in the flame, both
combustants and oxygen. A compensating factor can
be the composition of the tail gas stream. When it
mainly consists of hydrogen and CO, the burning will

20 initially convert the hydrogen to steam. This
process is very fast. The steam formed will undergo
a watergas shift to convert the CO into CO_2 and more
hydrogen. This process is also reasonably fast.
Only methane present may burn rather slowly. The

25 result can be a substantial increase in size. This
does not lead to a costly change of the turbine
combustor unit design in cases where sufficient
space is available. Wherein it may be necessary to
use a combustion chamber of increased volume it is

30 especially easy when an outside combustor unit is
used for the combustion. It is more difficult when

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the combustor unit is directly integrated with the first expander sector. Another possible solution in the use of highly diluted fuels would be the use of sintered high temperature catalysts to promote the

5   combustion in a limited space. For changing the combustor volume determination of the burning rate under the expected burning conditions will provide the necessary design input.

In normal turbine operations that amount of air

10   compressed in the compressor unit, whether to a pressure of 8, 12, 16 or higher absolute atmospheres, depending on the particular design of the turbine, is all supplied to the energy production unit either as oxidization gas 18 for

15   fuel combustion in the combustor unit or as cooling gas 20, 22 or 24 for temperature control of the combustion gas which is expanded through the first 32 and second 38 expanders of the production unit. Some gas turbines are designed for an air to fuel

20   ratio of 3:1 and some for 4:1, wherein the amount of air compressed by the compressor unit and supplied to the energy production unit is 3 times or 4 times that required to provide the stoichiometric quantity of oxygen required for complete oxidation of the

25   fuel. Accordingly, in 3:1 turbine design, which type turbines provide for air compression ratios of 12:1 to 16:1 or greater, for each mole per hour of methane fuel supplied about 30 moles per hour of air is compressed in the compressor unit; in a 4:1

30   turbine which provides for an air compression ratio of about 8:1, for each mole per hour of methane fuel

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about 40 moles per hour of air is compressed. In a
3:1 turbine, the mass imbalance between compressor
and energy production units is about 1.9%, in a 4:1
turbine it is about 1.4%, the imbalance reflecting
5   the addition of fuel to the energy production unit.
Accordingly, gas turbines are designed to
accommodate this mass imbalance, and as a safety
feature of a conventional performance design provide
for safe operation at an imbalance of up to 10%. A
10   gas turbine of conventional design must be operated
within this design constraint.

Accordingly, the amount of oxygen and nitrogen
which can be diverted from the compressor unit from
flowing to the energy production unit side in the
15   form of an oxygen enriched gas stream is limited in
quantity by this mass imbalance limitation of the
turbine thrust bearing unless means for making up
the deficiency to the mass balance so induced is
provided.

20   In addition to the mass balance constraint
which must be observed for proper gas turbine
operation, the designed thermal constraints of the
turbine must also be observed. The design of the
turbine requires that the temperature of the
25   combustion gases therein be closely matched to the
designed operating temperature which, depending on
the particular model of gas turbine utilized, ranges
from about 1700°F to 2050°F. Accordingly, the
design of a gas turbine assumes that all air
30   compressed in the compressor unit will be supplied
to the energy production unit and that the N_2 and

excess O_2 content thereof is available as cooling
gases to moderate and control the temperature of the
combusted fuel gas to the design temperature of the
gas turbine.

5   The diversion of a substantial quantity of O_2
and N_2 from the energy production unit in the form of
an oxygen enriched gas stream produced from the
compressed air stream from the compressor unit, if
not otherwise compensated for, will disrupt the mass
10   and thermal balance design of the turbine. If not
compensated for, then only small quantities of an
oxygen enriched gas stream could be recovered
without exceeding the mass balance safety tolerance
of the gas turbine even if a proper combustion
15   temperature is otherwise maintained.   This
invention comprises a method and apparatus for
recovering large quantities of an oxygen enriched
gas from the volume of a compressed air stream
produced by a gas turbine by compensation of the
20   mass loss to the energy production unit section
thereof by providing means for maintaining the
turbine in proper mass and thermal balance as the
turbine is utilized to provide the duty/power
requirements of a process which utilizes the oxygen
25   enriched gas stream as a reactant.

          The oxygen enriched gas can be used for
adiabatic reforming without a catalyst of
hydrocabonaceous materials, starting from methane
and ranging up to hydrocarbonaceous solid fuels like
30   sub-bituminous or standard coal. In one embodiment
of this invention the oxygen enriched gas stream is

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preferably utilized to adiabatically reform natural
gas to a nitrogen containing raw synthesis gas which
in turn is processed to convert a quantity of the CO
and H_2 thereof into a normally liquid or waxy

5   hydrocarbon product which is removed from the gas
phase to yield a residual gas stream balance i.e., a
tail gas, containing unreacted H_2, CO or a
hydrocarbon and that quantity of N_2 which was
introduced into the raw synthesis gas by the oxygen

10   enriched gas utilized to adiabatically reform the
natural gas. This tail gas is utilized as a fuel
gas for operation of the energy production unit of
the gas turbine as one means for maintaining a
tolerable mass balance between the compressor and

15   energy production units of the turbine since all
nitrogen initially diverted from the compressor unit
to energy production unit side thereof while
producing the oxygen enriched gas mixture is
returned to the energy production unit in the fuel

20   gas therefor. In alternative embodiments of the
inventive process, wherein the oxygen enriched gas
stream is utilized for other types of processing
which do not result in a tail gas stream suitable
for use as a fuel gas or wherein the tail gas

25   although of suitable heating value for fuel use has
been depleted in its nitrogen content -- such
processing, for example, being the use of the oxygen
enriched gas for more efficient operation of a Claus
Unit or for production of a synthesis gas utilized

30   in ammonia production -- mass balance between the
compressor and energy production units of the gas

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turbine is maintained by means of adding a non-combustible fluid such as low pressure stream to the energy production unit in an amount to balance against the amount of O_2 and N_2 lost to the energy production unit by such utilizations of the oxygen enriched gas stream.

In all embodiments, the excess power developed by the turbine over that required for production of the oxygen enriched gas stream is utilized to provide for the other duty requirements of the process, such as the operation of gas compressor or the generation of electrical energy.

The Oxygen Separation Unit

Figure 2 schematically illustrates a unit design wherein a gas turbine supplies compressed air to an air separation unit for the production of an enriched oxygen stream, which can be used in a process. Air 2 is fed through a filter 4 and passed by line 6 to the air compressor 8. The compressed air in line 10 is split in stream 17 and stream 50. Stream 17 is fed via heat exchanger 19, which serves to balance the temperature to burner 26. From the process unit 76 wherein the oxygen enriched air 68 is utilized a tail gas stream is fed via line 80 to the burner 26. This stream can be augmented in methane content by addition of natural gas through line 82. The tail gas stream is warmed up to a desired level in heat-exchanger 84, and then fed via line 86 to the burner 26.

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Stream 50 is heat-exchanged and further cooled
in heat exchangers 52 and 54, after which it is
filtered through a fine filter 56 before entering
via line 58 into the diffusor unit 60. Two streams
5   are generated here. Air enters the low pressure or
permeate side 64 of the diffusor unit via line 66
and lowers the oxygen partial pressure in this
sector, thus helping the diffusion of oxygen. This
air stream moves preferentially countercurrently to
10   the flow of the high pressure air, coming in via
line 58 to the non-permeate side 62 of the diffusor.
Stream 68 is obtained at low pressure, between 0.5
and 1 ata, and comprises an oxygen rich gas stream
containing appreciable amounts of nitrogen. Stream
15   68 is fed to the process unit 76, where it is
compressed before use. Compressors 44 and 46 which
are operated by the turbine by mechanical linkage 42
can be used for compression duties in the operation
of the process unit 76. The process 76 may also
20   produce a low pressure steam byproduct. Steam may
be taken by line 88 and, if necessary, admitted by
value 90 to mix with the tail gas in line 86. By
this means if the tail gas 82 is of an insufficient
mass to maintain the turbine with a proper mass
25   imbalance tolerance, additional mass may be added to
the bleed gas in the form of low pressure steam to
maintain a proper tolerance in the turbine. Stream
70 exits out of the diffusor at close to the inlet
pressure in line 58. This stream is passed by line
30   70 through heat exchanger 72 and thereafter fed by
line 74 to the combustor 26 via lines 20, 22 and 24

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to effect cooling of the combustion gases to a
designed temperature. Combustion gases are taken
out of the burner through line 30 and fed to a first
expander unit 32. In the first part of the expander

5   the gas expands and cools. The energy, made
available in this expansion, drives the expander
blades around thus rotating shaft 34. This shaft
drives compressor 8. Further, expansion of the hot
gas takes place in a second sector of the expander

10 38, which further expansion produces power for
compressors 44 and 46 through shaft 42. It is also
possible to use the power generated for producing
electricity. On the shaft between the air
compressor 8 and the first expander 32 is a thrust

15 bearing 36, which keeps the shaft in place against
the larger thrust of the expander against the
smaller thrust of the air compressor.

Preferably the diffusor unit 60 is a semi-
permeable membrane separator. Any of a number of

20 semi-permeable membranes may be used to effect
oxygen enrichment, including organic polymer
membranes and inorganic membranes. Organic polymer
membranes include those formed of polycarbonates,
polyesters, polyester carbonates, polysulfones,

25 polyolefins, polyphenylene oxides, polyphenylene
sulfides, polyethers, fluorinated polyamides,
polystyrenes, polyetherketones, polyetherether
ketones, polyetherimides, and polyamideimides. The
membrane may further be a polysiloxene thin film

30 such as that disclosed in Japanese Patent No. 59-
51321, or an aromatic condensed ring polyamide such

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as those disclosed in U.S. Patent No. 4,975,190,
which disclosures are also incorporated by
reference.

All membrane diffusor units 60 are protected by
5   very fine filters to eliminate very small particles,
which otherwise might clog the surface of the
membranes. Of the possible organic polymer
membranes, those that are suitable for use in the
invention should withstand a pressure differential
10   between the permeate and the non-permeated zones of
150 to 300 psig or greater within the temperature
range of 100 and 150°F, without extension,
compaction or collapse. In addition to the choice
of polymerized material, factors which also
15   contribute to the suitability of a membrane include
the molecular weight of the polymer used and the
manner in which the membrane is suspended. The
membrane may be mounted in the diffusor unit in a
plate-and-frame module, or a spiral-wound or
20   capillary module, and the choice of mounting will in
part determine the capability of the membrane to
withstand a pressure differential between the non-
permeate and the permeate zones. A capillary module
is preferred because it provides a large membrane
25   surface area and because the hollow fibers are
resistant to distortion or rupture by the pressure
differential across the membrane surface.

In an exemplary capillary module, the membrane
is formed into many hollow fibers. Hollow fibers
30   formed of a semipermeable membrane and having an
inner diameter of between 0.01 and 0.1 microns are

disclosed in U.S. Patent No. 4,955,993, which is
incorporated by reference. The fibers extend
through a housing and through a gas impermeable
barrier at each end of the housing. The fibers,

5   barriers and housing define a permeate and a non-
permeate zone. In a preferred mode, compressed air
from the compressor is supplied to the inside all of
the fibers and this interior constitutes the non-
permeate zone whereas the area exterior to the

10 fibers is the permeate zone. Oxygen diffuses
preferentially to the nitrogen through the wall of
the fibers and is collected in the permeate zone
around the fibers. It is also possible to have the
compressed air fed to the zone around the fibers

15 which, in this case, would constitute the non-
permeate zone, and collect the permeate inside the
fibers. This last method can lead to use of higher
pressures, but also calls for thicker fibers, which
have a slower diffusion rate. In this last method

20 oxygen in the air diffuses preferentially into the
hollow of the fibers and passes through the barrier
at one end via the fibers and is withdrawn into a
permeate zone.

        Where an organic membrane is used, it may be

25 necessary to cool the heated compressed air from the
gas turbine compressor before contacting the
compressed air with the membrane surface. Heat
exchangers such as 52 and 54 between the compressor
8 and the separator 60 may be used to cool the

30 compressed gas.

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Alternatively, a high temperature inorganic membrane may be used, such as, but not limited to, a silver composite membrane, a yttrium doped zirconium membrane or other solid oxide electrolyte membrane.

5 Wherein an inorganic membrane is used, the heated compressed gas may be contacted with the membrane at elevated temperature.

The oxygen selective membranes known to the art typically have selective factors of five or more.

10 When used to produce an oxygen enriched gas stream from air, the resultant oxygen enriched steam may have an oxygen content of up to 55 mole percent. Since under the preferred operating conditions, discussed below, the oxygen content of the oxygen

15 enriched gas stream is between about 30 and about 40 mole percent, a diluting gas, preferably air, is provided to dilute the oxygen content to within the preferred range. It is preferred to produce an oxygen enriched gas stream which is of 35 mole % or

20 less O_2. Gas streams richer in O_2 than 35 mole % generally require the use of compressors of special material construction for their safe compression which, if utilized, would add significantly to the capital cost of the equipment.

25 Preferably, air is introduced into the oxygen enriched permeate in the oxygen separator 60 via line 66 as stripper air. By diluting the oxygen enriched permeate at the surface of the semi-permeable membrane, the oxygen partial pressure

30 gradient across the membrane is maximized, thereby providing a greater driving force for the separation

of oxygen to the low pressure-permeate side of the
membrane. Consequently, a membrane of a given
surface area can permeate a greater quantity of
oxygen at a faster rate than otherwise obtainable
5   when dilution air is mixed with the enriched oxygen
permeate away from the membrane surface.

When the exemplary hollow fiber module is used,
the stripper air 66 is supplied to the permeate zone
outside the fibers (assuming the compressed air is
10   being fed to the insides of the fibers). The
stripper air moves countercurrently to the high-
pressure air flowing inside the fibers. The
produced mixture of permeate and stripping air exits
out of the permeate zone via line 68; which is
15   located close to the inlet site 58 of the
pressurized air.

In addition to oxygen content control, the
dilution or stripper air 66 provides a means of
controlling the nitrogen throughput of the process
20   76, which in turn provides a control means for the
mass balance of the gas turbine by a return of this
nitrogen to the turbine in the tail gas 80 as fuel
to burner 26.   Oxygen removed from the
compressed air of the turbine compressor by
25   diffusion into the oxygen enriched permeate gas will
ultimately be consumed by a chemical reaction and
will not be returned to the energy production unit
of the turbine in the tail gas fuel even though all
co-diffused nitrogen is so returned. Stripper air
30   66 utilized to operate the membrane diffuser 60 more
efficiently provides a means for replacing the mass

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loss due to oxygen diversion/consumption by
replacing that mass loss with about an equivalent
mass of nitrogen while providing a final oxygen
enriched gas of the preferred oxygen concentration

5   of 35 mole %. For instance, for an exact mass
replacement, the membrane unit 60 may be operated to
provide a permeate gas stream of 43.889 mole % O_2.
For each 1000 SCFH of such permeate gas the addition
thereto of 634.929 SCFH of air (21% O_2 and 79% N_2)

10 provides as a final gas product 1634.929 SCFH of 35
mole % oxygen content, or 572.225 SCFH of oxygen.
Of this amount 438.890 SCFH of oxygen is provided by
the permeate gas whereas the stripper air has
provided the additional oxygen together with 501.594

15 SCFH of nitrogen. The mass of this nitrogen
(molecular weight of 28) leads to an equivalent
oxygen mass (molecular weight of 32) of 438.894 SCFH
of oxygen. For all practical purposes the added
nitrogen is equal in mass to that of the oxygen in

20 the permeate. The additional nitrogen passes as an
inert through the subsequent processing unit 76
wherein the permeate oxygen is consumed and this
additional nitrogen is ultimately returned in the
tail gas fuel 80 to the combustor unit 26 of the

25 turbine wherein its mass exactly compensates for
that mass of oxygen lost to the permeate gas stream.

Adiabatic Reforming

Figure 3 is a schematic continuation of Figure

30 2. The oxygen rich gas stream 68, is compressed in
compressor 44. It exits from that compressor via

line 100. Natural gas stream is fed via line 45 to
compressor 46, from which it exits through line 102.
Streams 100 and 102 are combined in adiabatic
reformer 104, where they react over a reforming
5 catalyst to form a raw synthesis gas. Small amounts
of steam and/or CO_2 may be added to the reactor. The
raw synthesis gas leaves through line 106 and are
cooled in heat exchangers 112 and 116. In Figure 3
a third turbine driven compressor 122 is shown,
10 which may provide additional compression, as needed,
to the raw synthesis gas. In many cases this may
not be necessary. Then the compressed synthesis gas
enters a process unit 76. The process unit
produces products, leaving via line 78 and a tail
15 gas, leaving for the combustor 26 via line 80.

In the adiabatic reforming process of Figure 3
natural gas is reacted with a quantity of gas which
is enriched with oxygen relative to air to convert
the hydrocarbon content of the natural gas to carbon
20 monoxide, carbon dioxide, hydrogen and water wherein
the molar ratio of hydrogen to carbon monoxide
(H_2/CO) is between about 1.5 and about 1.9 and the
molar ratio of carbon monoxide to carbon dioxide
(CO/CO_2) is between about 10 and about 25. The raw
25 synthesis gas stream resulting from this reaction,
on a water free basis, comprises from about 15 to
about 48 mole % nitrogen, from about 30 to about 50
mole % hydrogen, from about 18 to about 30 mole %
carbon monoxide, and the balance being carbon
30 dioxide, and a residual unreacted hydrocarbon
content of less than about

5 mole %.

The raw synthesis gas stream 106 is then
utilized in other processing steps 76 to produce
various products 78 which are recovered to leave a
5   tail gas 80 which is returned as fuel to the gas
turbine combustor 26.

The oxygen enriched gas utilized to produce
such reformed gas contains greater than about 21
mole % oxygen and at least about 40 mole % nitrogen.
10   Such an oxygen enriched gas is adiabatically reacted
with a carbonaceous material, like coal, heavy oil,
naphtha or methane. When methane is used as
carbonaceous material, the reaction can be carried
out either in the absence or in the presence of a
15   reforming catalyst to produce a reformed gas of a
composition similar to the one given above. These
gases are produced at a temperature of from about
1800 to about 2500 °F and a pressure of from about
300 to about 2000 psig. Preferably the adiabatic
20   reaction of natural gas is accomplished by
compressing the oxygen enriched gas to a pressure of
from about 310 to about 2010 psig then heating the
compressed oxygen enriched gas to a temperature of
from about 700 to about 1400°F and passing it into
25   admixture with a natural gas stream which has the
same pressure level and heated to a temperature of
from about 800 to about 1050°F. In order to avoid
the need to use compressors of a special material
construction, it is preferred to utilize an oxygen
30   enriched gas wherein oxygen is present in an amount
less than 35 mole %.

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Wherein the so compressed and heated mixture of
natural gas and oxygen enriched gas is adiabatically
reacted in the absence of a catalyst, it is
necessary that the natural gas and oxygen enriched
5   gas be formed so that the produced reformed gas has
a final temperature of from about 2100 to about
2500°F. At such conditions, an adiabatic reaction
between the hydrocarbon content of the natural gas,
and oxygen will occur in the absence of a catalyst
10   to yield a reformed gas stream having the above
mentioned final temperature and a pressure of from
about 1 to about 10 psi lower than that of the
unreacted intake gas. Wherein the adiabatic
reaction is performed in the presence of a reforming
15   catalyst, the natural gas and oxygen enriched gas
may be formed so that the produced reformed gas has
an outlet temperature of from about 1800 to about
2200°F and a pressure of from about 100 to about
2000 psig.
20   For the embodiment of this process which uses a
reforming catalyst in the formation of a reformed
gas, the catalyst composition may be any of the well
known reforming catalysts, compositions as, for
instance, described in Petrochemical Handbook '89,
25   Hydrocarbon Processing, November 1989, page 106,
which is incorporated herein by reference.
         The quantity of the oxygen for reaction with
the natural gas must be selected such that on
reaction, after contact with a reforming catalyst or
30   with sufficient residence time at reaction
temperature without a reforming catalyst, the

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reformed gas reaches the desired final temperature
of between 1800 and 2500°F. On the basis of
hydrocarbon carbon content of the natural gas, the
CO and CO_2 content of the reformed gas is more than
5   80 mole %, preferably more than 90 % CO. Between 1
and 15 mole % of the original hydrocarbon carbon
atoms of the natural gas stream are present in the
reformed gas as methane. In addition, the reformed
gas will have a substantial amount of nitrogen
10   originating from the oxygen enriched gas stream. An
additional product of the reforming process is
water. The process significant reactants and
products of the adiabatic reforming step may be
represented in the following manner, it being
15   understood by one of ordinary skill that the
stoichiometric relationships are not expressed and
where parentheses indicate wholly or partially
unreacted components:

$$(N_2+CH_4) +CH_4+O_2 \rightarrow CO+CO_2+H_2O+H_2+ (N_2+CH_4)$$
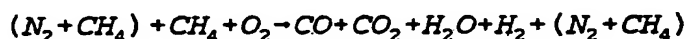
The reformed product is thus a raw synthesis
20   gas whose primary components are carbon monoxide and
hydrogen, but which also typically contains some CO_2,
wherein the raw synthesis gas is comixed with water
vapor, nitrogen and unreacted methane. When no
steam or CO_2 have been added to the reaction, the
25   reformed gas stream contains H_2 in a molar ratio with
respect to CO of from about 1.5 to about 1.9 and CO
is present in a molar ratio with respect to CO_2 of
from about 10 to about 25.

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Process Utilization of the Nitrogen Containing Synthesis Gas

To render the raw synthesis gas suitable for commercial production of liquid hydrocarbons by an MTG process, the raw synthesis gas must first be dewatered. The gas is cooled to a temperature of from about 100 to about 140°F to condense and remove water therefrom. At a temperature of about 100°F, the final vapor pressure of water is about 0.95 psia, at a temperature of about 140°F the final water vapor pressure is about 2.89 psia. Depending on the pressure, cooling to 140°F will remove from the raw synthesis gas most of the water produced in the reforming reaction.

The so refined synthesis gas may be used for the production of liquid hydrocarbons by converting the synthesis gas to methanol or a methanol-dimethylether mixture with subsequent conversion of the methanol or methanol-ether mixture to high molecular weight hydrocarbons using process pioneered by Mobil Oil Corp. and described in U.S. Patent Nos. 4,044,061 and 4,058,576.

To produce the starting material for the methanol to gasoline conversion process ("MTG"), the dewatered or refined synthesis gas is reheated to a temperature of from about 435 to about 500°F and passed into contact with a catalyst composition which promotes reaction between hydrogen and carbon monoxide to produce methoxy compounds, particularly methanol and/or dimethyl ether or combinations thereof. Catalysts suitable for such reaction are

well known. Examples of such catalysts compositions
are described in U.S. Patent 4,520,216, which
discusses both the catalyst to make methanol only
and catalyst mixtures for coproduction of methanol
5   in admixture with DME. This patent is hereby
incorporated by reference.

Preferably, the refined synthesis gas is
contacted with such methoxy compound production
catalysts at a pressure of from about 390 to about
10   1990 psig. Accordingly, wherein the methoxy
catalyst composition is one for production of
methanol only, it is preferred to initially produce
the raw synthesis gas under conditions wherein the
resulting synthesis gas has a pressure of from about
15   600 to about 1990 psig. This manner of producing
the synthesis gas eliminates the need to recompress
it to the pressure required for the most efficient
conversion of the synthesis gas to methanol by
contact with the catalyst. Wherein the catalyst
20   composition is one which promotes the co-production
of methanol and dimethyl ether, the synthesis gas
may be reacted at a pressure of from about 560 to
about 1500 psig. At such lower pressures, the
conversion of the synthesis gas carbon content to
25   methanol and dimethyl ether is still efficient even
though the pressure is significantly lower. Wherein
the synthesis gas is initially produced to a
pressure of from about 100 to about 2000 psig, it is
preferred to contact it with a methanol/DME
30   catalysts since for such contact, the synthesis gas
requires only a moderate degree of recompression

before contact and, accordingly, both the size and
cost of the required compressor for such operation
is lower.

Methanol Production

5   One embodiment of the method of this invention
contemplates the recovery of the hydrocarbon content
of a natural gas in the form of crude methanol only.
Since methanol is a liquid, it may be conveniently
10 stored and transported to an offsite location for
subsequent processing, such as refining into market
grade methanol, for use in manufacturing methyl
ethers or for use as the feed stream to an offsite
methanol to olefin or gasoline process.

15 The preferred method for recovering methanol
only from a synthesis gas made in accordance with
this invention is described in commonly owned
copending U.S. Patent Application Serial No.
508,928, which is hereby incorporated by reference.
20 With reference to figure 3 of that application, it
is also possible to react the final gas after
reaction in the third methanol reactor described in
Serial No. 508,928 and after removal of most of the
methanol made by cooling, over a mixed
25 methanolacidic catalyst to promote the formation of
DME. This DME, together with small amounts of
methanol formed, can be extracted with water and
converted in the presence of CO_2 and steam into a
small amount of synthesis gas, that is a mixture of
30 CO and hydrogen, plus extra CO_2. This synthesis gas,
made by recycle, is added to the gas, fed to the
first methanol reactor. Thus a considerably higher

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methanol yield can be attained, notwithstanding the
relatively low partial pressures of the reactants.

Fuel Production

Methanol to Gasoline

Another embodiment of the invention
contemplates the production of gasoline from a
methanol-DME mixture and this intended use
determines the conditions most preferred for the
synthesis gas production.

The method most preferred for gasoline
production from a synthesis gas made in accordance
with this invention is described with particular
reference to figure 4 of commonly owned U.S. Patent
Application Serial No. 508,928 which is incorporated
by reference.

Once again, utilization of the process tail gas
as fuel for the gas turbine returns it to a proper
mass balance by returning to the energy production
unit thereof all nitrogen which was initially
diverted into the O_2 enriched gas stream. This means
by itself enables the production of an O_2 enriched
gas stream in greater volume than otherwise would
allow compliance with the mass balance constraints
of the gas turbine. Further, as described with
reference to Figure 2, since in the preferred mode
stripper air 66 is added in an amount to dilute the
O_2 enriched permeate to an O_2 level of not greater
than about 35 mole % O_2, a further quantity of both
O_2 and N_2 are obtained in the O_2 enriched stream 68
with the so added N_2 being returned in the tail gas

80 to the turbine. This further increases the amount of permeate O_2 which can be produced without violating the mass balance constraints of the turbine.

Although the preferred embodiments of the process have been described with reference to the production of crude methanol only and with regard to methanol and gasoline, the process is not so limited. Other molecular sieve catalyst compositions, as described in U.S. Patent No. 4,788,369 may be employed in place of a MTG catalyst for the production of other desirable compositions from methanol and/or DME, like for instance that proposed in U.S. Patent No. 4,654,453 wherein excess isobutane produced in the MTG process is reacted with olefins made in the MTG process. This more complicated scheme has merit from the standpoint of octane improvement.

Fischer-Tropsch/Hydrofining Fuel Production

Another embodiment of this process, as illustrated in Figure 4, utilizes the raw synthesis for the production of diesel grade liquid hydrocarbon by reacting it under Fischer-Tropsch conditions to a waxy hydrocarbon which is then hydrocracked to a diesel grade liquid hydrocarbon.

In this embodiment the raw synthesis gas is first reacted under water-gas shift reaction conditions until a quantity of its CO and H_2O content has reacted to CO_2 and H_2 to provide a shifted synthesis gas having a ratio of H_2 to CO of from

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about 1.85 to about 2.2, most preferably about
2.1:1. The shifted synthesis gas can then be
contacted with a medium selective for the absorption
of CO_2 and its CO_2 content may be reduced to about 1

5   mole %.

Figure 4 schematically illustrates a unit
design wherein a nitrogen containing synthesis gas
as produced by the unit illustrated by Figure 2,
after compression, is fed by line 200 into unit 202

10   where a small watergas shift is achieved. The gas
exits via line 204, is cooled in heat exchanger 205
and then the gas and condensed liquid are fed via
line 208 into separator 212. Condensed liquid is
separated and taken off via line 210. The gas moves

15   via line 207 to CO_2 absorber 206, where the gas is
contacted with a standard carbon dioxide absorber
liquid, like for instance an amine. The fat
solution is separated at the bottom and via valve
211 and line 212 fed into stripper 214. There CO_2 is

20   removed by the input of heat at the bottom (heat
exchanger 218) and leaves the stripper in line 224.
The stripped liquid is cooled and recycled to the
absorber via line 216, cooler 220 and pump 222. The
gas with a much lower CO_2 content exits from the

25   absorber via line 226 and is fed to the first
Fischer-Tropsch reactor 228. Heavy and waxy
products are separated hot in separator 236, as
stream 235, while lower hydrocarbons are obtained as
liquids by cooling in heat-exchanger 238 and

30   separated in separator 250. These liquids are taken
away via line 256. The remaining gas is reduced to

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an intermediate pressure and combined via line 252
and valve 254 with the earlier separated CO_2 after
that gas has been cooled in heat-exchanger 225 and
compressed in compressor 260. Also steam is added

5   via line 264. The combined stream is heated in heat
exchanger 268 and fed via line 270 to heat-exchanged
reformer 280, which is heated by the hot gas coming
out of the adiabatic reformer (unit 104 of Figure
3), which produced the first synthesis gas. All the

10   reformed gas from unit 280 is combined into line
282, is heat exchanged and cooled in heat exchangers
284 and 270 and fed via line 272 into separator 274.
There an aqueous condensate is removed via line 276.
The gas is taken from the separator by line 275 and

15   compressed in compressor 278, and via line 280
heated in heat exchanger 281 then contacted with a
standard carbon dioxide absorber liquid in a second
CO_2 absorber unit 290. The gas from which CO_2 has
been removed is the taken by line 282 and fed into

20   the second Fischer-Tropsch reactor 300, after the
products of the first stage Fischer-Tropsch reaction
have been added to this gas via lines 235 and 256.
After this second reaction the gas and liquid
mixture is taken via line 301 warmed up in heat

25   exchanger 302 and fed by line 304 to hydrogenator
306. There the waxy products are hydrogenated into
lower boiling and commercially more attractive
hydrocarbon streams, like Diesel and kerosene. The
exit stream from reactor 306 is fed via line 307 to

30   heat exchangers 308 and 312, which cool the gas
down. Condensates are removed in separator 316 and

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fed by line 318 to a distillation sector for final
splitting. With reference to Figures 2 and 4, the
remaining gas stream is fed out of separator 316 via
line 80 to the burner 26 of the gas turbine after
5   addition of some natural gas by line 82 to augment
the fuel value of the gas.

        Other Process Uses for Products
        Yet another embodiment of this invention
10   contemplates the use of the O_2 enriched gas stream
for the production of non-hydrocarbon products, such
as ammonia, or for increasing the efficiencies of
oxidation based processes, such as the Claus
process. In many Claus processes a gas turbine is
15   already present for the purposes of power,
mechanical or electrical generation. As before
described, with reference to Figure 2, an oxygen
separation unit, such as a semi-permeable membrane
unit, may be incorporated into the compressed air
20   line between the compressor and energy production
units of the turbine and an O_2 enriched gas stream
may be produced with the O_2 depleted gas stream being
returned to the energy production unit of the
turbine.
25   The O_2 enriched gas stream thereby produced can
be utilized as the oxidizing gas in the Claus
process to increase the throughput capacity of the
plant and reduce plant emissions. In this event, a
tail gas suitable for use as turbine fuel is not
30   produced and consequently the mass of nitrogen
diverted from the energy production unit of the

turbine as a part of the O_2 enriched gas stream is
not returned to the turbine. In this circumstance,
as shown in Figure 2, the means for returning the
turbine to a proper mass balance comprises the
5 addition of low pressure steam by line 88 to the
energy production unit of the turbine in an amount
necessary to insure a mass imbalance of no greater
than 10%. Low pressure steam is invariably available
as a byproduct of the Claus process.

10 In another embodiment, the O_2 enriched gas
stream is utilized to produce a high N_2 content
synthesis gas which may be utilized to produce
ammonia. In this circumstance, the nitrogen content
of the gas stream is consumed in the production of
15 ammonia. Accordingly, that quantity of N_2 initially
diverted from the energy production unit is
substantially depleted by its conversion to ammonia
and is not returned to the energy production unit as
part of the tail gas fuel. Again, a means for
20 restoring the turbine to a tolerable mass balance is
to add low pressure steam or other non-combustible
fluid to the energy production unit. Again low
pressure steam is almost always available as a
byproduct in an ammonia production process.

25

Means For Maintaining Turbine Mass
and Thermal Balance

In whatever overall process the gas turbine-
30 oxygen separation unit may be incorporated for the
purposes of power generation and production of an O_2
enriched gas stream as a process reactant, the mass

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and thermal balance of the turbine must be
maintained within tolerances. · One way for achieving
such maintenance is by limiting the quantities of
the O_2 enriched gas stream taken to such minor
5   amounts as to lack any substantial utility to an
industrial scale process. To increase the
quantities of an O_2 enriched gas stream that may be
produced to amounts which have industrial scale
utility, means for matching the mass-thermal balance
10   of the turbine as a function of the quantity of O_2
enriched gas stream produced, must be provided.

As described, this invention provides means for
maintaining a gas turbine in proper mass-thermal
balance while producing large quantities of an O_2
15   enriched gas at significantly reduced cost, both
capital and operating, for the amounts of O_2 so
produced. One embodiment of such means comprises
the utilization of such O_2 enriched gas to produce a
synthesis gas containing at least that quantity of N_2
20   diverted from the turbine compressed air which is
integrated with a process that converts such
synthesis gas to recoverable hydrocarbon products
and a tail gas and use of such tail gas as fuel for
said turbine to Ththereby return to the energy
25   production unit of the turbine all N_2 initially
diverted therefrom. Such means increases the
quantity of O_2 which can be produced by returning to
the turbine all nitrogen initially co-diverted.

Another means comprises the addition of diluent
30   air to the O_2 enriched permeate gas stream to result
in a product stream of not greater than 35 mole % O_2,

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the dilute air so added adding both additional O_2 and
additional N_2, increasing both the total quantity of
O_2 possible to permeate and total resultant O_2
available as well as the total quantity of N_2 in the
5   resulting O_2 enriched gas stream, utilization of this
gas stream to form a synthesis gas which is then
converted to a recoverable hydrocarbon product and a
tail gas stream and use of such tail gas stream as
fuel for the energy production unit of the turbine
10   to thereby return to such unit the total quantity of
N_2 imparted to the synthesis gas. This means
provides for a return to the energy production unit
of the turbine all N_2 diverted from the turbine
compressed air and an additional N_2 quantity added by
15   the diluent air. Accordingly, the quantity of O_2
which can be separated from the turbine compressed
air is increased by the amount of N_2 added by diluent
air without violating the mass balance constraints
of the gas turbine design.
20   In another embodiment, the means for conforming
to the mass balance constraints of the gas turbine
to conform with the large quantity of O_2 enriched gas
produced comprises the addition to the energy
production unit thereof of a compensating mass of a
25   non-combustible fluid, such as CO_2 or low pressure
stream equal to the mass of O_2 and N_2 diverted from
the energy production unit in the form of the O_2
enriched gas stream so produced and utilized in a
process without provision for return of any part
30   thereof to the energy production unit as fuel or
otherwise.

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The Examples

The Examples which follow demonstrate, but are
not limiting of, the invention herein described. In
each example, unless otherwise stated, MPH means lb-
5 moles per hour and SCFH means the cubic feet of a
gas per hour measured on the basis of 760 mm Hg and
0°C. MTPD means metric tons per day. Although the
actual composition of air is about 21 mole % O_2, 78
mole % N_2, and 1 mole % other gases; Air, for
10 purposes of the examples, assumes a mixture of 21
mole % O_2 and 79 mole % N_2. Unless otherwise
indicated, for purposes of the examples, it is
assumed that the oxygen separation device comprises
a semi-permeable membrane which is selective to the
15 permeation of O_2 over N_2 to a gas permeation factor
of about 5.6.

EXAMPLES

Example 1 (Comparative)

20 A standard membrane diffusor unit for enriched
air uses 6200 SCFH of air. This air is compressed
to 8 atmospheres gauge or 9 atmospheres absolute and
then fed to the diffusion unit. There 2600 SCFH of
a permeate gas is produced at atmospheric pressure
25 which contains 40 mole % of oxygen. The non-
permeate gas has an oxygen content of 7.278 %. The
purity of oxygen reached in the diffused or permeate
gas corresponds to approximately an enrichment
factor of oxygen over nitrogen of 5.6. If it is
30 desired to use 35% oxygen content gas, 928.6 SCFH

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air are added to the permeate gas stream in order to
obtain 3528.6 SCFH 35 % oxygen.

Example 2

5   This example illustrates the gain in production
of oxygen-rich gas out of a diffusor by feeding the
diffusor with compressed air, when such air feed can
be used in larger amounts than in Example 1, due to
its "free" availability. The gain in diffusor

10   effectivity is obtained notwithstanding the somewhat
lower pressure of the compressed air, following the
8 to 1 compression ratio of the gas turbine used.
The amount of oxygen and nitrogen diffused out of
the compressed air is limited to a total, which will

15   only slightly disturb the mass balance around the
gas turbine. In this example a Frame-5 General
Electric gas turbine generates about 36000 BHP on
its shaft by feeding it with a fuel gas stream
having the equivalent heating value of 884.4 MPH

20   methane. For the fuel supplied this turbine
compresses 33691 MPH air to 8 atmospheres absolute
(ATA) in the compressor unit of the gas turbine.
This amount of air contains 4 times the amount of
oxygen necessary to completely oxidize the methane

25   fed. Of the compressed air 9265 MPH, or about 10%
excess over stoichiometry for complete fuel
combustion, is directly fed back to the burner, to
which the methane is fed. The rest of the
compressed air, 24426 MPH, cooled to a temperature

30   of 100 °F and then fed to 564 diffusor units, each
containing the same total membrane surface area as

the unit of Example 1. Due to the larger air flow at the lower pressure it is preferred to have a shorter pass for the high-pressure non-permeate gas, keeping the total surface area the same. The exit

5 high-pressure gas, or "spent air," amounts for each diffusion unit to 13882 SCFH, containing 16.0% oxygen. Each diffusor produces 2531.3 SCFH of an oxygen-rich permeate gas with an oxygen content of 48.42%. For the 564 diffusor units this corresponds

10 to about 456 MTPD equialent pure oxygen.

The oxygen-rich permeate gas is diluted with air to a total of 4957.7 SCFH of a 35% oxygen gas mixture per each diffusion unit, which is a substantial increase of the amount prepared with a

15 comparable diffusor unit under Example 1. All the 35% oxygen streams are combined and used in processes as discussed in the text. The gas turbine remains driven by natural gas. Notwithstanding the seemingly small amount of diffused product, the mass

20 balance indicates a shortage of 1451.7 lb./hr. in the energy producing unit, more than the allowable 10% difference with a reversed thrust bearing. This amount of weight is made up by the same amount of weight of steam, which is fed to the turbine at 10

25 ata. Alternatively, a greater amount of steam could be added to provide for a greater mass flow in the energy production unit than in the air compressor unit, in which event the thrust bearing need not be reversed.

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Example 3

The same gas turbine as in Example 2 likewise
supplies 9265 MPH of compressed air to the flame and
the rest, 24426 MPH of compressed air, is fed to 462

5   diffusional units, each with the same diffusional
area as in the earlier Examples. Each unit
therefore is fed with approximately 20038 SCFH of
compressed air. 3160 SCFH of 1 ata air is used to
strip the diffused product out. Obtained are 5861.4

10   SCFH, containing 35.79% of oxygen. Diluting this
with some more air results in 6192.3 SCFH of 35%
air. This number is still substantially higher than
in Example 2. Total equivalent oxygen production is
467 MTPD, which signifies a substantial increase in

15   equivalent oxygen produced per diffusion unit.

Because of the relative improvement in the
oxygen diffusion, thanks to the stripping air, the
mass balance now is only 8.75% off, so that no steam
needs to be injected, after the reversal of the

20   thrust bearing. Alternatively, the thrust bearing
need not be reversed if steam is adde in an amount
to provide for a greater mass flow in the energy
prodution unit than there is in the air compressor
unit.

25

Example 4

In this example the air feed pressure is
increased to 11.2 ATA by compressing the cooled air
out of the gas turbine and after compression cooling

30   the gas back down. Now only 287 membrane diffusor
units are used, each with the same membrane surface

area as in the earlier Examples, but with
substantially shorter fiber lengths. Each unit now
receives a total of 32256 SCFH of compressed air.
Spent air at 28422.5 SCFH per unit, contains 16.92%
5   oxygen. The product stream per unit, is 3833.5
SCFH, containing 51.26% oxygen. Now the total
equivalent oxygen is 388 MTPD.

By dilution with air 8285.8 SCFH of a 35%
oxygen stream is obtained per unit. Steam is added
10   after reversal of the thrust bearing to bring mass
balance within 10%.

Example 5

A similar run as in Example 4 but operated at
15   about 0.5 ATA lower pressures, both on the non-
permeate side as on the permeate side of each
diffusor unit produces an oxygen concentration in
the product stream of 53.74%.

Similar improvements as shown in these Examples
20   can be obtained with diffusion materials which have
different enrichment factors for oxygen over
nitrogen.

Example 6

25   In this Example a gas turbine is fed by a tail
gas stream of a methanol process, containing 1516
MPH CO, 2126 MPH H_2, 100 MPH CO_2, 550 MPH CH_4, 11766
MPH N_2 and small amounts of water. The total fuel
value of this gas stream corresponds to that in
30   1725.86 MPH methane, which leads in a 3/1 turbine to
a total compressed oxygen volume of 10355 MPH and a

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compressed air volume of 49310 MPH. These lower air
excess turbines are of higher efficiency. They
operate at 12/1 or 16/1 air compression ratio. The
fuel value of the tail gas is 97.66 BTU/SCF.

5   Out of the total amount of compressed air 32950
MPH are fed to a diffusor complex after compression
of the gas to 13 ATA. Stripper air is used to an
amount of 9184 MPH. Obtained are 17570 MPH of 34.74
% oxygen content, which stream is used in the

10   methanol production process after compression from
its level of 1 ATA to 87 ATA. Diffusion is
economical, in that the production of oxygen
equivalent is 2.59 times faster than in the standard
preparation of 40% oxygen as per comparative Example

15   1. This comparison is based on the determination of
the comparable amount of 34.7% oxygen-rich gas,
which amount is obtained by mixing in air with the
richer oxygen-containing stream. The total
equivalent oxygen is 1066.8 MTPD.

20   The feed gas to the reformer reactor,
containing 9100 MPH methane, 500 MPH ethane, 300 MPH
CO_2, and 300 MPH nitrogen, is also compressed to this
pressure. The two gases are mixed after individual
preheats and reacted in a reformer over reforming

25   catalyst to provide a raw synthesis gas at a final
temperature of 2100 degrees Fahrenheit.

          After cooling and removal of water the refined
synthesis gas is reacted in sequence in three
methanol reactors with intermediate removal of

30   methanol. Then the remaining gas is fed to a
reactor filled with a mixture of a methanol catalyst

and a simple acidic one, like alumina. In this
manner conversion of methanol formed to dimethyl
ether (DME) is catalyzed. This DME formation allows
a much larger conversion of the synthesis gas.

5   Now DME and methanol are absorbed out leaving a
tail gas stream which is fed to the gas turbine as
fuel. After regasification of the DME and methanol
which has been absorbed out of steam and CO_2 are
added to this gas mixture the gases are reformed at
10   modest temperatures to a mixture, comprising CO and
hydrogen. This reformed gas mixture is added to the
raw synthesis gas made by adiabatic reforming.
Balance around the gas turbine.

                Air used is 1,422,100 lb./Hr.
15   Gas fed to the diffusor is 950,278 lb/Hr.
                Back to the gas turbine is "spent air",
                weight 698,769 lb/Hr.
                Loss in these two streams is 251,509
                lb/Hr.

20

                Final bleed gas weight is 389,348 lb/Hr.
                Total leads to a total weight of
                1422100 - 251509 + 389348 = 1559949 lb/Hr.
          Ratio of mass is 1.097, which is less than the
25   10% mass balance limitation within the turbine must
be operated.
          For combustion of the tail gas is needed
(1516 + 2126 + 4 x 550) = 5842 pound atoms oxygen,
or 2921 MPH. This corresponds to 13910 MPH air.
30   Available are 16360 MPH air for combustion, which is
more than sufficient.

Example 7

This Example addresses the use of the diffusor
in combination with a gas turbine for use in a
Fischer-Tropsch process.

5   The gas turbine is fed with a tail gas to
which, extra methane is added to arrive at a
composition comprising 1325 MPH CH_4 and 11141 MPH
Nitrogen. This gas has a combustion value of 96.6
BTU/scf. The gas turbine is of the 4/1 compression
10   variety. The total volume of compressed air
provided by the turbine compressor is 50476 MPH.

Of this air stream 35380 MPH are fed after
cooling to a temperature not exceeding 110 °F to a
diffusor unit after compression to 9 ATA. 9957 MPH
15   air are used as diffusor stripper air at 0.7 ATA.
Obtained from the permeate side of the diffusor are
16260 MPH of an oxygen-nitrogen mixture containing
33.33% oxygen. The comparative production rate is
now 2.007 times the standard rate. Total equivalent
20   oxygen produced is 885.9 MTPD.

This oxygen enriched gas stream is compressed
and used in a Fischer-Tropsch process.

First the gas stream is contacted after preheat
to 800° F with a natural gas stream, containing 9100
25   MPH methane, 500 MPH ethane, 300 MPH CO_2 and 300 MPH
nitrogen. The reaction is catalyzed by a high-
temperature reforming catalyst. Pressure of the
reforming operation is 32.3 ATA. The hot raw
synthesis gas composition is 8910 MPH CO, 16090 MPH
30   hydrogen, 490 MPH CO_2, 1610 MPH water, 1000 MPH
methane, and 11141 MPH nitrogen.

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This raw synthesis gas is cooled and subjected
to some watergas shift to effect a watergas shift of
500 MPH CO with water to 500 MPH CO_2 and 500 MPH
hydrogen.   The shifted synthesis gas is cooled,
5   water is removed, and then the shifted synthesis gas
is contacted with a CO_2 absorber fluid.

After removal of the CO_2 the synthesis gas is
compressed to 57 ATA and contacted with a Fischer-
Tropsch catalyst.   The catalyst is chosen so as to
10   generate a large fraction of a waxy hydrocarbon
product.   Produucts are removed first hot, then by
cooling.   The contact with a Fischer-Tropsch catayst
is repeated, followed by a second recovery.   After
separation of waxy product the remaining gas is
15   dropped in pressure and reformed over a reforming
catalyst after addition of the extracted CO_2 and of
steam.   This reforming can take place at least
partly in heat-exchange with the hot gases out of
the adiabatic reformer step, as the pressure of
20   operation is essentially the same, namely 32.83 ATA.

After cooling, watergas shift and further
cooling the CO_2 is removed and the remaining gas now
contains 2045 MPH CO, 4895 MPH H_2, 11141 MPH
nitrogen, and traces of water.   This gas is
25   compressed to 57 ATA and fed to a second stage of
reheated contact with a catalyst to produce a second
quantity of a waxy hydrocarbon product Fischer-
Tropsch.

After the Fischer-Tropsch reaction the first
30   waxy product is added to this reaction gas stream
and the combined stream is contacted with a

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hydrogenation catalyst in order to convert the waxy
fraction into lower boiling products like diesel and
kerosene. After final removal of the products the
remaining bleed gas stream contains only 840 MPH
methane and that amount of N₂ which was originally
present in the raw synthesis gas. 485 MPH methane
are added in order to arrive at sufficient fuel for
the gas turbine, this in order to drive the
different compressors in the process.

This final tail gas is fed to the gas turbine.
Gas Turbine Balance:

Air to Compressor

$50480 \times 28.84 = 1,455,728$ lb./Hr.

Total Product Out of Diffusor

$1/3 \times 16260 \times 32 + 2/3 \times 16260 \times 28 = 476,960$
lb./Hr.

Stripping air to Diffusor

$9957 \times 28.84 = \underline{287,160}$ lb./Hr.

Diffused O₂/N₂   189,800 lb./Hr.

Fuel Mass

$1325 \times 16 + 11141 \times 28 = 333,148$ lb./Hr.

Mass Increase Therefore

143,348 lb./Hr. or 9.85% of flow to

compressor.

Example 8

This Example shows how the gas turbine -
diffusor combination might be used in an ammonia
process. As the adiabatic reforming process leads
to a relatively high nitrogen content, the only
possible ammonia processing is based on use of low
hydrogen to nitrogen operation. Catalysts have to

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be used, that can make this acceptable. The
ruthenium-based catalysts can operate under such
conditions.

5   The gas turbine is fed with a bleed gas out of
the ammonia process. It contains 4912 MPH hydrogen,
4954 MPH nitrogen, and 399 MPH methane, next to
small amounts of argon. This gas has a combustion
lower heat value of 649.4 MM BTU/Hr. and a specific
heating value of 167 BTU/SCF.

10   The gas turbine is on a 3 air excess basis,
compressing the air to 12 ATA. The total air stream
is 53625 MPH. After compression 33070 MPH air are
fed to the diffusor unit. There 8550 MPH air are
used to strip. The product of diffusion is a stream

15   of 17850 MPH oxygen-nitrogen mixture with 34.71%
oxygen, representing an oxygen equivalent of 1081
MTPD. This stream is produced at a rate per surface
area which is 2.13 times the rate that a standard
diffusor using compressed air to 9 ATA will produce,

20   using the same membrane quality. The reason for the
improved rates result from the higher oxygen
concentration left remaining in the non-permeate gas
stream (10.7% as against the standard of 7.28%
commonly used) and the use of stripper air in the

25   permeate zone of the diffusor, this combined with
the slightly higher pressure of operation The
partial pressure of oxygen in the spent air is 1.25
ATA.

        The oxygen-rich stream is compressed to 36 ATA,
30   preheated to 800°F and reacted with a natural gas
stream, consisting of 9100 MPH methane, 500 MPH

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ethane, 300 MPH nitrogen and 300 MPH carbon dioxide, preheated to 1050°F. A reforming catalyst is used to achieve proper reaction. The final temperature is 2100°F and the pressure is 34.95 ATA.

5   The gas is quenched with condensate, more steam is added to a total of 25000 MPH. High and low temperature watergas shift contacts are taken, resulting in a gas stream containing 129 MPH CO. After cooling and removal of condensate, CO_2 is

10   removed by extraction. The remaining gas is subjected to methanation. All these steps are common in processing of raw synthesis gas for use in ammonia manufacture.

       After cooling and removal of the remaining

15   water the gas composition is 25912 MPH H_2, 11954 MPH N_2, and 399 methane, and traces of argon.

       This gas is fed to a standard ammonia loop, containing, however, a modern catalyst, like ruthenium on carbon. The tail gas out of the loop

20   contains 4912 MPH H_2, 4954 N_2, 399 MPH methane and traces of argon. This tail gas stream is fed back to the gas turbine. The process makes 14000 MPH of ammonia.

       The oxygen process is an example for a very

25   low-cost ammonia plant with a somewhat higher than usual consumption of natural gas.

       If desired, some steam reforming with indirect heat input can be driven by the heat from the adiabatic reforming. Then at somewhat higher

30   capital cost a low consumption of natural gas is encountered.

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Gas Turbine Balance:

      Air to compressor

          $53625 \times 28.84 = 1,546,545$ lb./Hr.

      Total product out of diffusor

5    $17850 \times .3471 \times 32 + 17850 \times .6529 \times 28 = 524,583$ lb./Hr.

      Stripping Air to Diffusor

                  8550×28.84 = <u>246,582</u> lb./Hr.

                 Diffused O_2/N_2 = 278,001 lb./Hr.

      Fuel mass

10      $4912 \times 2 + 4954 \times 28 + 399 \times 16$ = <u>154.920</u> lb./Hr.

                      Less   = 123,081 lb./Hr.

This is 7.96% of air mass flow to compressor. This
is allowable with a reversal of the thrust bearing.

15

<u>Example 9</u>

    This Example shows how the diffusor can be
added to a gas turbine dedicated to generate
horsepower, for example in generating electricity.
20   The thus generated rich oxygen-nitrogen mixture can
be used for many purposes. For instance, it can be
used in general in many combustion process, thus
because of its lower nitrogen content the amount of
stackgas is diminished. In this Example it is
25   assumed it is used to replace air feed in a Claus
process. This is a variation of the well-known
proposal to replace air by oxygen in an existing
Claus unit in order to increase production rate
and/or lessen the sulfur dioxide output. Most of
30   the possible reduction in nitrogen content of the

effluent of the Claus unit is obtainable by using a
rich oxygen-nitrogen mixture.

A gas turbine is fed by 1930 MPH methane. The
efficient machine operates on a 3/1 ratio of air

5   over stoichiometric air and compresses this air to
about 12 ATA. The total amount of air compressed is
55143 MPH. Of this air part is fed to the combustor
part of the 67 expander (internal or external). The
rest of the air, 33840 MPH, is fed to a diffusor

10   unit.

The diffusor unit produced 8990 MPH oxygen-
nitrogen mixture, containing 46.8% oxygen. The
productivity of the membrane is 2.029 times that of
a membrane, working under standard conditions. This

15   comparison is made on basis of diluting products
with air down to 34.7 oxygen content and then
comparing productivity at this level. It should be
pointed out, that under standard conditions, only
40% oxygen content is reached.

20   If no corrections were made, the mass flow to
the expander side of the gas turbine is only 85.04%
of that fed to the compressor side. To bring the
difference down below 10%, 4375 MPH of steam are
added. This steam could be made available from the

25   Claus unit as it is constantly generating steam in
its hydrogen sulfide burner. Also, the thrust
bearing has to be reversed.

Although the invention has been described with
reference to its preferred embodiments those skilled

30   in the art may appreciate from such description
various other embodiments and modifications of the

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invention which do not depart in scope or spirit from the invention as described and claimed hereafter.

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What is claimed is:

1.   1.   A method for preparing a gas stream
2. containing nitrogen which contains greater than 21
3. mole % oxygen with a gas turbine comprising an air
4. compressor unit and an energy production unit
5. comprising a combustor unit and a first expander
6. mechanically linked to the air compression unit by a
7. shaft carrying a thrust bearing, comprising the
8. steps of:
9.   (a)   compressing air in a compressor unit
10. of a gas turbine;
11.   (b)   contacting at least a portion of such
12. compressed air with a means which is preferential
13. for the separation of O_2 from said pressurized air to
14. produce two separable gas streams, one being
15. enriched in O_2 relative to nitrogen and a second gas
16. stream which is depleted in O_2 relative to nitrogen;
17.   (c)   passing said oxygen depleted gas
18. stream to the combustor unit of said turbine;
19.   (d)   recovering said O_2 enriched gas stream
20. in an amount which exceeds in mass that amount which
21. can be diverted from the energy production unit
22. without exceeding the maximum thrust bearing design
23. tolerance; and
24.   (e)   maintaining a mass flow within the
25. energy production unit in an amount which is within
26. the maximum thrust bearing design tolerance by means
27. for adding a non-combustible fluid to said energy
28. production unit.
29.

1   2.   The method of claim 1, wherein said means
2   for preferentially separating O_2 from air comprises a
3   semi-permeable membrane which is selective to a
4   permeation of oxygen relative to nitrogen to produce
5   in a low pressure permeate zone an oxygen enriched
6   permeate gas stream and in a high pressure non-
7   permeate zone an oxygen depleted non-permeate gas
8   stream.

1   3.   The method of claim 2, wherein said semi-
2   permeable membrane has a gas permeability value of O_2
3   which is at least about 5 times greater than for N_2.

1   4.   The process of claim 3, wherein the oxygen
2   depleted non-permeate gas stream has a partial
3   pressure of O_2 of at least about 0.8 atmospheres
4   absolute.

1   5.   The method of claim 2, further comprising
2   the step of passing a quantity of air through the
3   permeate zone to strip the oxygen enriched permeate
4   therefrom to produce as a resultant stream an O_2
5   enriched gas stream having an O_2 content not
6   exceeding about 35 % O_2.

1   6.   The method of claim 1, wherein the non-
2   combustible fluid is low pressure steam.

1   7.   The method of claim 1, wherein the non-
2   combustible fluid is nitrogen.

1   8.   The method of claim 1, wherein the
2 tolerance of said thrust is designed for a 10%
3 greater mass bearing flow in said energy production
4 unit than that in the air compression unit.

1   9.   The method of claim 7 wherein said
2 nitrogen is contained in a gas stream which is
3 supplied to the combustor as fuel.

1   10.   The method of claim 2, wherein a portion
2 of the air compressed in the compressor unit is
3 supplied to the combustor unit in a quantity
4 containing oxygen in an amount stoichiometrically
5 sufficient to completely oxidize all oxidizable
6 components in a source of fuel which is supplied to
7 the combustor unit.

1   11.   The method of claim 1, further comprising
2 the steps of:
3   (f)   reacting said O_2 enriched gas stream
4 with a source of carbon to produce a gas product
5 stream containing H_2, CO and N_2;
6   (g)   converting at least a portion of the
7 H_2 and CO content of the gas product stream into a
8 normally non-gaseous carbon containing compound;
9   (h)   separating the normally non-gaseous
10 carbon containing compound from the converted gas
11 product stream to yield as a balance a gas stream
12 containing N_2 oxidizable gaseous compounds; and
13   (i)   returning said gas stream balance as
14 fuel to the energy production unit of said turbine
15 and by such means returning nitrogen to the energy

16 production unit in a compensating quantity to that
17 amount of nitrogen diverted from the energy
18 production unit in the O_2 enriched gas stream.

1   12.   The method of claim 11, wherein said means
2   for preferentially separating O_2 from air comprises a
3   semi-permeable membrane which is selective to a
4   permeation of oxygen relative to nitrogen to produce
5   in a low pressure permeate zone an oxygen enriched
6   permeate gas stream and in a high pressure non-
7   permeate zone an oxygen depleted non-permeate gas
8   stream.

1   13.   The method of claim 2, further comprising
2   the step of passing a quantity of air through the
3   permeate zone to strip the oxygen enriched permeate
4   therefrom to produce as a resultant stream an O_2
5   enriched gas stream having an O_2 content not
6   exceeding about 35 mole % O_2.

1   14.   The method of claim 12, further comprising
2   the step of passing a quantity of air through the
3   permeate zone to strip the oxygen enriched permeate
4   therefrom to produce as a resultant stream an O_2
5   enriched gas stream having an O_2 content not
6   exceeding about 35 mole % O_2.

1   15.   The method of claim 14, wherein said
2   stripping air is provided in a quantity such that
3   the number of moles of N_2 thereby added to the O_2
4   enriched gas stream compensates in mass for that

5　quantity of oxygen removed from the O_2 enriched gas

6　stream in the form of water and non-gaseous

7　hydrocarbon product.

1　　　16.　The method of claim 1, further comprising

2　the steps of:

3　　　　　(j)　reacting said O_2 enriched gas stream

4　with a source of carbon to produce a gas product

5　stream containing H_2, CO and N_2;

6　　　　　(k)　converting at least a portion of the

7　H_2 and N_2 content of the gas product into ammonia;

8　　　　　(l)　separating ammonia from the converted

9　gas stream to yield as a balance a gas stream

10　containing unreacted N_2, H_2 and methane.

11　　　　　(m)　adding an additional amount of

12　methane to said gas stream balance in a quantity to

13　provide a total BTU/scf value to the gas to enable

14　its use for return to the energy production unit as

15　fuel, and

16　　　　　(n)　adding low pressure steam to the

17　energy production unit in a quantity sufficient to

18　compensate for mass flow lost to the energy

19　production unit as O_2 and N_2 consumed from the O_2

20　enriched gas stream during its utilization in the

21　production of ammonia.

1　　　17.　The method of claim 11, wherein a portion

2　of the H_2 and CO content of said gas product stream

3　is converted into a normally liquid carbon

4　containing compound by:

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5   (g') removing water from the gas product
6   stream, and
7   (g") contacting the gas product stream
8   with a catalyst composition which promotes reaction
9   between H_2 and CO to produce a quantity of a methoxy
10 compound.

1   18.   The method of claim 17, further comprising
2   the step of
3   (g''') contacting said methoxy compound
4   with a molecular sieve catalyst composition to
5   convert the methoxy compound into a normally liquid
6   hydrocarbon compound.

1   19.   The method of claim 11, wherein a portion
2   of the H_2 and CO content of said gas product stream
3   is converted into a normally liquid hydrocarbon
4   compound by
5   (g^1) subjecting said gas product stream to
6   a water-gas shift reaction to provide a shifted gas
7   stream wherein the ratio of H_2 to CO of from about
8   1.85 to about 2.2;
9   (g^2) removing CO_2 from said shifted gas
10 stream;
11   (g^3) reacting the shifted gas stream under
12 Fischer-Tropsch reaction conditions to convert a
13 portion of its H_2 and CO content to a normally waxy
14 hydrocarbon;
15   (g^4) separating the waxy hydrocarbon from
16 the gas stream;

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17 (g⁵) adding CO_2 and steam to the gas

18 stream;

19 (g⁶) reforming the gas stream to increase

20 the H_2 content thereof;

21 (g⁷) returning the waxy hydrocarbon to the

22 gas stream;

23 (g⁸) reacting the gas stream under

24 Fischer-Tropsch reaction conditions to convert a

25 portion of its H_2 and CO content to a normally waxy

26 hydrocarbon;

27 (g⁹) hydrofining the gas stream to crack

28 the normally waxy hydrocarbon content thereof to a

29 normally liquid hydrocarbon content; and

30 (g¹⁰) recovering the normally liquid

31 hydrocarbons from said gas stream to yield as a

32 balance in the gas stream methane and nitrogen.

1 20. A method for preparing a gas stream

2 containing nitrogen which contains greater than 21

3 mole % oxygen with a gas turbine comprising an air

4 compressor and a energy production unit, comprising

5 the steps of:

6 (a) compressing air in a compressor unit

7 of a gas turbine;

8 (b) contacting at least a portion of such

9 compressed air with a means which is preferential

10 for the separation of O_2 from said pressurized air to

11 produce two separable gas streams, one being

12 enriched in O_2 relative to nitrogen and a second gas

13 stream which is depleted in O_2 relative to nitrogen;

14   (c)   recovering said O_2 enriched gas stream
15   from said O_2 depleted gas stream;
16   (d)   passing said oxygen depleted gas
17   stream to the energy production unit of said turbine
18   in a quantity sufficient to contain an amount of
19   oxygen to completely oxidize fuel supplied to the
20   energy production unit; and
21   (e)   maintaining mass flow within the
22   energy production unit of said turbine to within a
23   limit of about 100 to 110% of mass flow within the
24   compressor unit of said turbine by means for adding
25   a non-combustible fluid to said energy production
26   unit in a quantity sufficient to compensate for the
27   mass flow lost to said energy production unit as
28   oxygen and nitrogen diverted therefrom by the
29   recovery of said O_2 enriched gas stream.

1   21. A method for preparing a gas stream
2   containing nitrogen which contains greater than 21
3   mole % oxygen with a gas turbine comprising an air
4   compressor unit and an energy production unit
5   comprising a combustor unit and a first expander
6   mechanically linked to the air compression unit by a
7   shaft carrying a thrust bearing, comprising the
8   steps of:
9   (a)   compressing air in a compressor unit
10   of a gas turbine;
11   (b)   contacting at least a portion of such
12   compressed air with a means which is preferential
13   for the separation of O_2 from said pressurized air to
14   produce two separable gas streams, one being

90

15   enriched in O_2 relative to nitrogen and a second gas

16   stream which is depleted in O_2 relative to nitrogen;

17   (c)   passing said oxygen depleted gas

18   stream to the combustor unit of said turbine;

19   (d)   recovering said O_2 enriched gas

20   stream; and

21   (e)   maintaining a mass flow within the

22   energy production unit in an amount which is within

23   the maximum thrust bearing design tolerance by means

24   for adding a non-combustible fluid to said energy

25   production unit.

1   22.   The method of claim 21, wherein the means

2   for the separation of oxygen separates at least 40%

3   of the oxygen content of the compressed air

4   contacted therewith.

1   23.   The method of claim 23, wherein at least

2   50% of the oxygen content is separated.

1   24.   The method of claim 22, wherein the means

2   for the separation of oxygen is a pressure swing

3   absorber.

1   25.   The method of claim 21, wherein the thrust

2   bearing of said turbine is positioned to accommodate

3   a larger mass flow in the air compressor unit than

4   exists in the energy production unit.

1   26.   The method of claim 21, further comprising

2   the step of controlling the turbine inlet

3   temperature (TIT) to a temperature within 200°F of

4   and not exceeding the maximum TIT of the turbine
5   design.

1   27.   The method of claim 26 wherein the TIT is
2   controlled by contolling the temperature of all gas
3   streams supplied to the combustor unit.
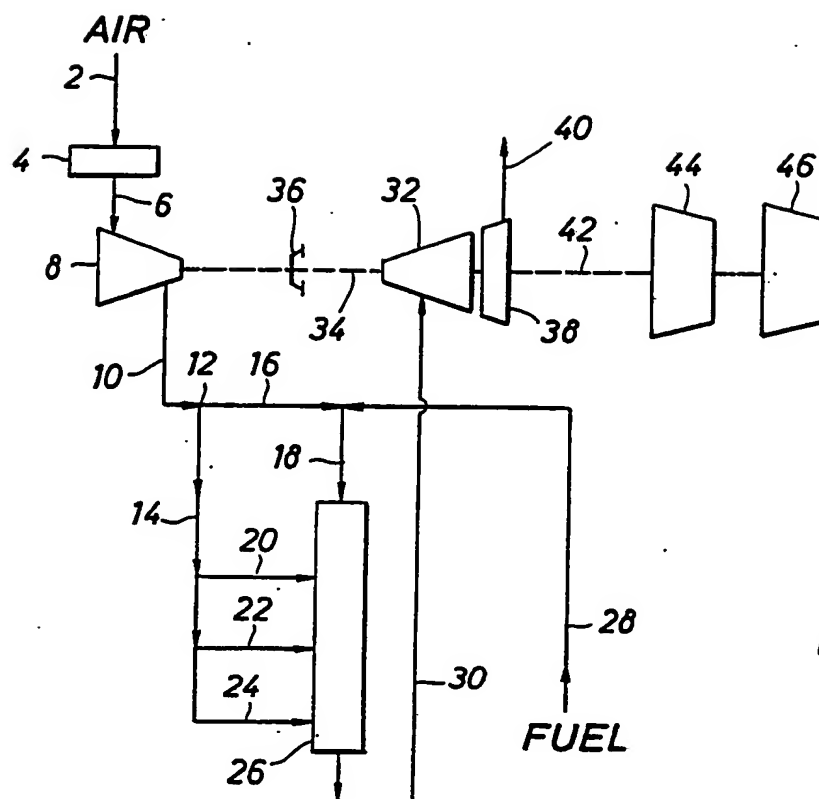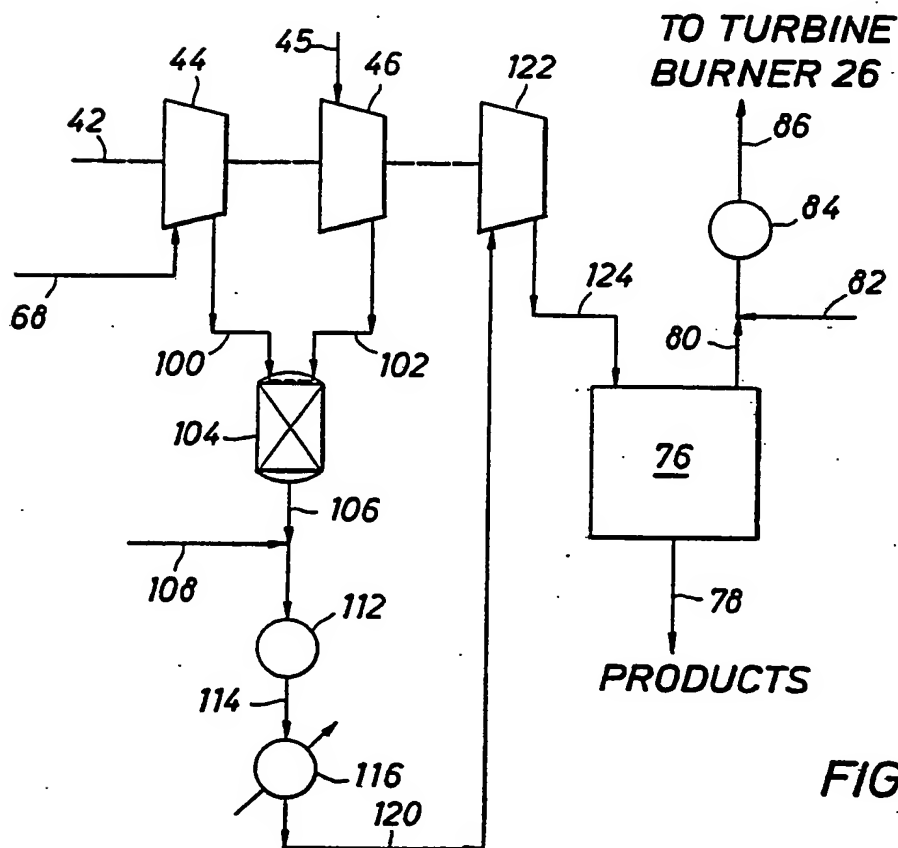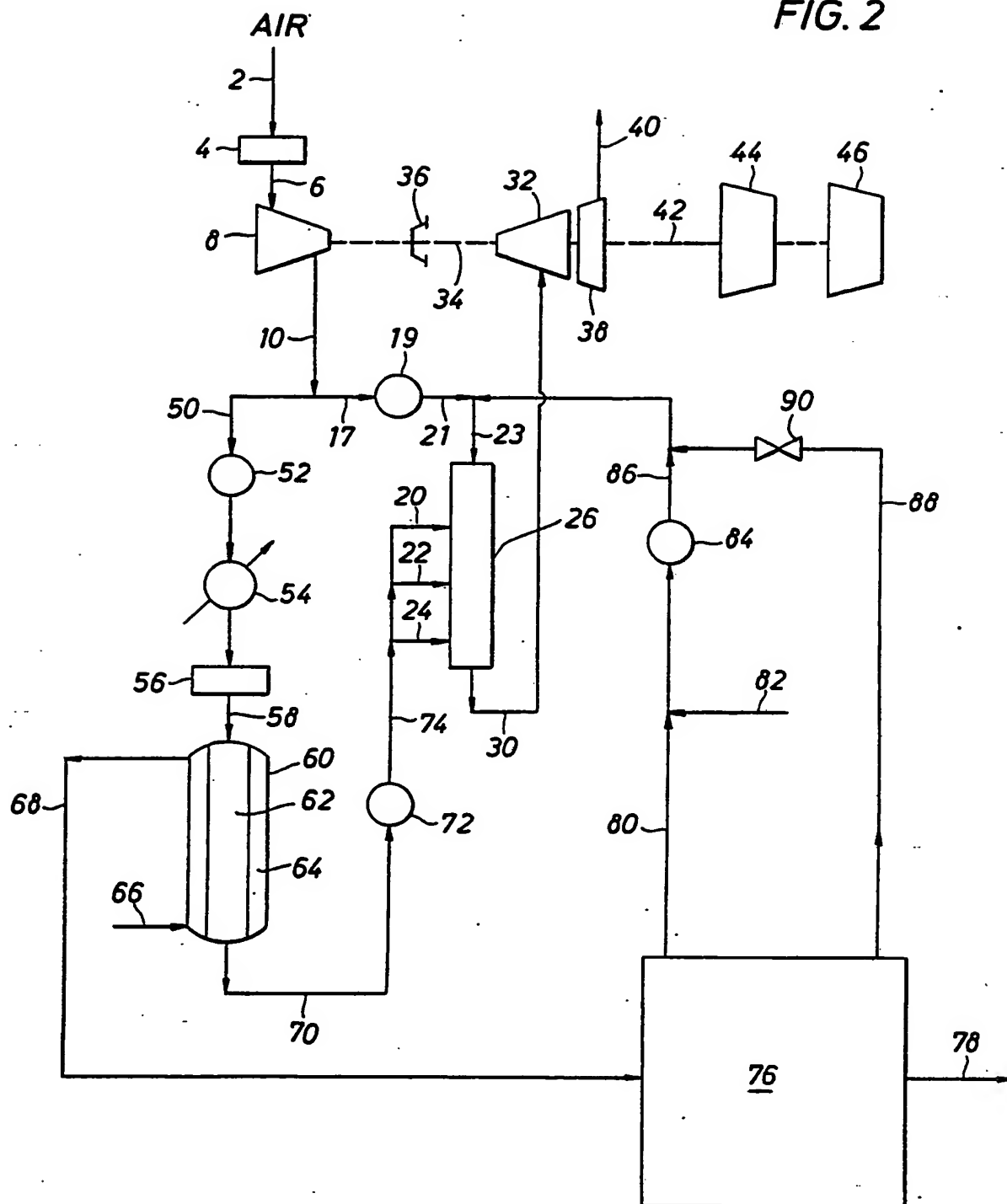
AIR

FIG.1

FUEL

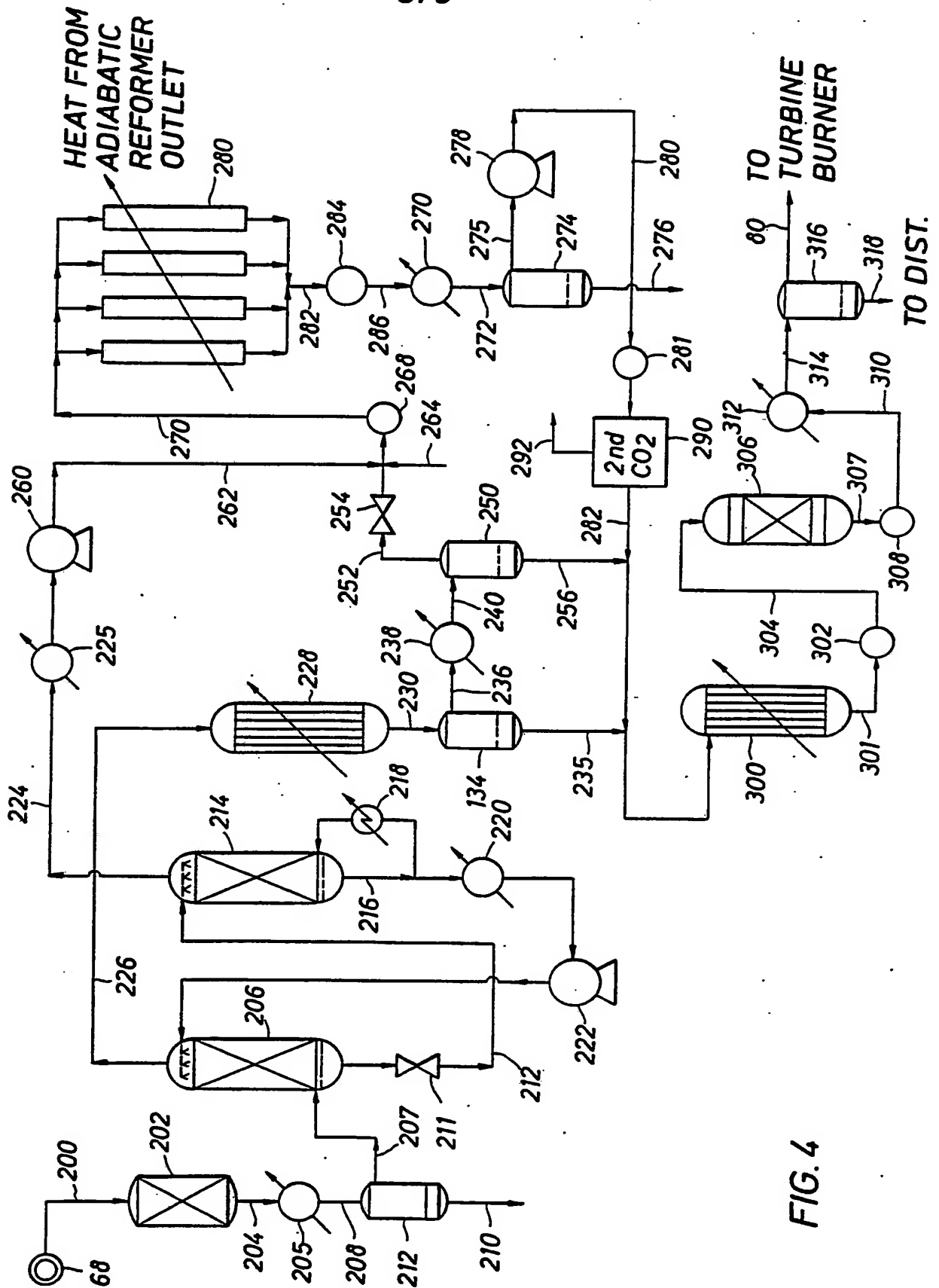TO TURBINE
BURNER 26

PRODUCTS

FIG.3

SUBSTITUTE SHEET

AIR

FIG. 2

FIG. 4

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C01B 21/00; C07C 1/04

US CL :518/702,703;585/408,606,733,946

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. :

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Gas Turbine Aps: And Fischer Tropsch and Oxygen enriched and air compress? And Combust?

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A, 4,545,787 (Hegarty) 08 October 1985 See col. 2, lines 55-68; col. 3, lines 1-63.	1-27
A	US,A, 4,973,453 (Agee) 27 November 1990 See col. 2, lines 35-65; See cols. 9 and 10 in their entirety.	1-27
Y	US,A, 5,023,276 (Yarrington et al.) 11 June 1991. See col. 3, lines 1-66; col. 4 in its entirety.	1-27

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be part of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 OCTOBER 1992	09 DEC 1992

Name and mailing address of the ISA/ Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer ANTHONY MCFARLANE
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